UNIVERSIDAD AUTÓNOMA DE MADRID

FACULTAD DE CIENCIAS

EVALUACIÓN AMBIENTAL DEL MUNICIPIO DE VILLAVICENCIO, (COLOMBIA), MEDIANTE EL ANÁLISIS DEL CONTENIDO Y VARIABILIDAD ESPACIAL DE METALES PESADOS EN POLVO VIAL URBANO Y DE LOS SUELOS IRRIGADOS CON AGUAS RESIDUALES

JUAN MANUEL TRUJILLO GONZÁLEZ

Tesis Doctoral

Madrid, octubre de 2018

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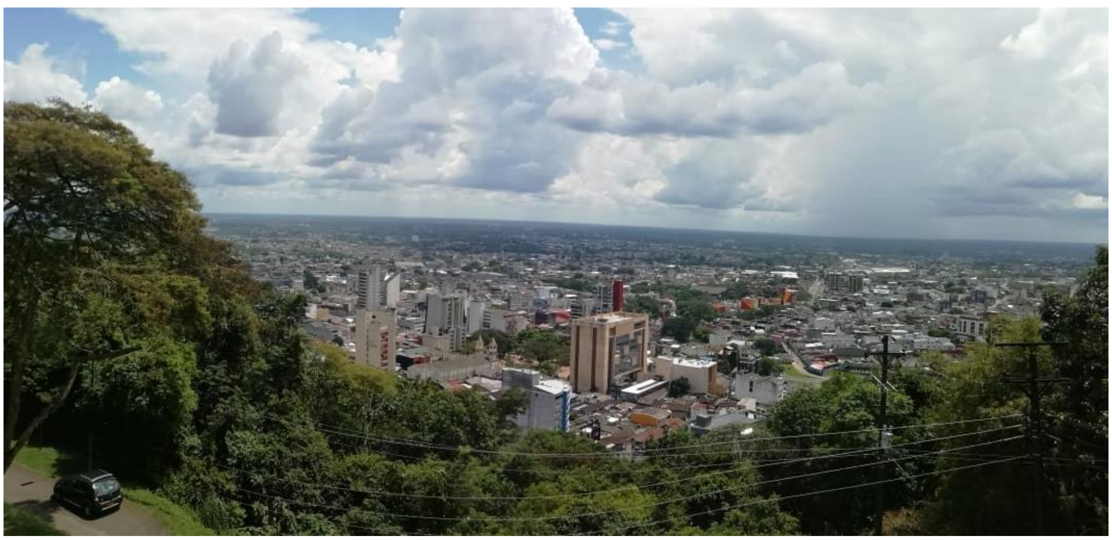

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Tesis Doctoral
2018

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La presente tesis doctoral se ha realizado al amparo del proyecto “Hot-spots o zonas riesgo por la presencia de metales pesados en sedimentos viales en la ciudad de Villavicencio”, financiado por la Dirección General de Investigaciones DGI de la Universidad de los Llanos, bajo el número CO1-F02-018-2016.

Para llevar a cabo este trabajo se ha realizado una estancia en el Instituto de Ciencias Ambientales de la Orinoquia Colombiana de la Universidad de los Llanos, Villavicencio, Colombia, entre los meses de diciembre de 2017 a julio de 2018. Así mismo se ha realizado una estancia de corta duración en la Universidad Autónoma de Madrid durante los meses de junio y julio de 2016.

A mis papás, por el esfuerzo que han tenido para para mi formación personal y profesional

A mis hermanos y a mis sobrinos que se han convertido en el motor de mi vida. A Tatianita, Vanesita, Camilita, Juanita, Danielito y Cristian

A mis amigos y compañeros que siempre estuvieron ahí dándome ánimo para continuar

AGRADECIMIENTOS

La presente investigación se ha realizado en el Grupo de Investigación en Gestión Ambiental Sostenible (GIGAS) del Instituto de Ciencias Ambientales de la Orinoquia Colombiana de la Universidad de los Llanos, coordinado por el Dr. Marco Aurelio Torres Mora; gracias especialmente por el soporte financiero que permitieron que desarrollara este proceso de investigación.

Al Dr. Raimundo Jiménez Ballesta, director y tutor de esta Tesis, por su confianza, dedicación, orientación y sobre todo por esas palabras de ánimo y comprensión que permitieron culminar el proceso.

A la Dr. Francisco Jesús García Navarro, co-director de este trabajo, su confianza y apoyo.

Al profesor Dr. Eric Brevik, Departments of Natural Sciences and Agriculture and Technical Studies, Dickinson State University, Dickinson, ND, USA, a la profesora Dra. Saskia Deborah Keesstra de Wageningen Environmental Research, Team Soil, Water and Land Use y al profesor Dr. Jin Zhang, Institute of Groundwater and Earth Sciences, JinanUniversity, Por todos sus aportes especialmente en el análisis de los resultados.

A mis amigos y colaboradores en la toma de muestras y al personal del laboratorio de Consultas Industriales de la Universidad Industrial de Santander (UIS) por su colaboración y apoyo siempre.

Un agradecimiento muy especial agradecimiento a mi amigo Dr. Marco Aurelio Torres Mora director del Instituto de Ciencias Ambientales de la Orinoquia Colombiana –ICAOC de la Universidad de los Llanos, por ser el principal promotor en mi crecimiento personal, profesional y científico.

Y en general a todos los investigadores y personal técnico del Grupo de Investigación en Gestión Ambiental Sostenible (GIGAS) y del Instituto de Ciencias Ambientales de la Orinoquia Colombiana (ICAOC) por todo el apoyo que recibí durante el desarrollo de esta investigación.

A todos muchas gracias.

RESUMEN

Los entornos urbanos de las ciudades de tamaño medio de América Latina albergan a más del 85% de la población. Esta concentración conlleva, entre otros, a múltiples actividades comerciales y un alto flujo vehicular, provocando un aumento de la contaminación ambiental urbana. En efecto, las carreteras se han convertido en el reservorio de contaminantes inorgánicos, tales como los denominados actualmente elementos potencialmente tóxicos (PTEx), que incluyen, entre otros, los metales pesados. Esta concentración de elementos supone fundamentalmente un factor de riesgo para la salud humana, pero también para los recursos naturales que ofertan importantes servicios ecosistémicos, sobre los que juegan un papel importante el suelo y el agua.

Por lo tanto, dado que existe una tendencia al incremento poblacional y que la dinámica de este tipo de ciudades responde precisamente ha dicho incremento, y dada la carencia de verdaderos procesos de planificación urbanística, el problema de la acumulación de PTEx tiende a incrementarse, aunque silenciosamente. Un ejemplo de la carencia de planificación se encuentra en la falta de tratamiento de las aguas pluviales que trasladan contaminantes a zonas periurbanas, pudiendo afectar especialmente a sus suelos agrícolas al cambiar su condición fisicoquímica.

En respuesta a esta problemática, desde las dos últimas décadas se vienen haciendo una serie de estudios encaminados a investigar cuales son las concentraciones y los patrones de distribución de estos PTEx en polvos viales (suelos/sedimentos o polvos de carretera, RD Road dust en inglés), así como los riesgos que representan tanto ecológicos como para la salud humana.

La ciudad de Villavicencio en Colombia, configurada como una ciudad de tamaño medio con alrededor de 500.00 habitantes, para el 2017, se le considera como una de las ciudades con crecimiento acelerado, debido a que en ésta se concentra el punto de entrada y salida a la región de la Orinoquia, configurándose en una nueva geografía económica ligada a sectores como el minero, energético y agroindustrial del país. Con esta perspectiva, se realizó un estudio para analizar los metales pesados presentes en el polvo de carretera en el área urbana de Villavicencio, abordando al mismo tiempo la posible influencia sobre los suelos agrícolas periurbanos. Para ello, se identificó y evaluó la concentración y distribución espacial de cinco metales pesados, Plomo (Pb), Cromo (Cr), Cadmio (Cd), Zinc (Zn), Cobre (Cu), ya que a escala mundial son considerados como unos de los más problemáticos. Su análisis, que se efectuó mediante técnicas de espectrofotometría de absorción atómica, fue llevado a cabo en el polvo de carretera de áreas urbanas de Villavicencio, partiendo de la premisa de dividir el territorio que conforma la ciudad en subáreas en función de los distintos usos del suelo. Adicionalmente se efectuó un análisis de riesgo.

Por otra parte, dado que la zona periurbana de Villavicencio se dedica parcialmente a uso agrícola, se consideró conveniente abordar el reconocimiento de dichos metales pesados en los suelos sometidos a tal uso, ya que cabe la posibilidad de que estos metales provenientes del polvo urbano puedan migrar a través de las aguas pluviales a dichos suelos agrícolas. Por tal motivo, posteriormente se tomaron muestras de suelo para analizar en laboratorio los contenidos de tales elementos y adicionalmente, se determinaron las características de interés agronómico de dichos suelos.

Los resultados obtenidos del polvo de carretera en tres zonas de la ciudad con diferente actividad funcional (zona residencial, zona comercial y zona de carretera) se encontró que las concentraciones promedio de metales pesados (expresados en mg/kg) siguieron las siguientes secuencias para cada una de las zonas comercial Pb (1289,4); Cu (490,2); Zn (387,6); Cr (60.2); Ni (54.3); de carretera Zn (133,3); Cu (126,3); Pb (87,5); Cr (9,4); Ni (5,3); residencial Zn (108,3); Pb (26,0); Cu (23,7); Cr (7,3); Ni (7.2).

Con el ánimo de discriminar los valores obtenidos se aplicó el denominado índice de geoacumulación, (I-geo), de cuya aplicación pudo deducirse que la zona comercial estaba fuertemente contaminada, mientras las otras dos zonas se incluyen en la categoría no contaminada. Del mismo modo, utilizando el índice de riesgo ecológico, la zona comercial se clasifica dentro de la categoría catalogada como de mayor riesgo, mientras que la de carretera y urbana se clasificaron como de bajo riesgo. En cuanto a los análisis de riesgo a la salud humana no alcanzaron los niveles de riesgo. La prueba de Kruskal-Wallis H, sugirió que el tipo de uso de la tierra tiene una influencia significativa en la variación espacial de los metales permitiendo identificar dos fuentes potenciales, una en función de su origen geoquímico y otra en función de la actividad vehicular.

Por su parte, en el análisis del suelo de los campos agrícolas periurbanos irrigados con agua de río potencialmente contaminadas con aportes de la escorrentía pluvial proveniente de la ciudad, presentan concentraciones de metales pesados por debajo de los límites de cuantificación, por lo que no están contaminados; de igual forma no se encontraron alteraciones sustanciales que evidenciaran un cambio o efecto relacionado con estos aportes. Este hecho puede estar asociado con los factores climáticos (temperatura y precipitación), que contribuyen a la rápida degradación de la materia orgánica y la casi ausencia de la misma, por lo que su función de retención de nutrientes y metales pesados es casi nula. Además, la intensa lluvia (más de 3000 mm/año), tiene una enorme capacidad de exportar los metales pesados, si bien, algunos serán absorbidos por las plantas.

Finalmente, se concluye que los datos reportados pueden facilitar la identificación de puntos calientes de contaminación con metales en las áreas urbanas, información que se convierte en una herramienta crucial para los procesos de planificación y de gestión ambiental urbana. Aunque en los suelos agrícolas del área periurbana de la ciudad de Villavicencio no se encontraron cambios sustanciales, es importante mantener un esquema de seguimiento y monitoreo para controlar y así poder tomar decisiones tempranas que garanticen la conservación del recurso, al tiempo que se eviten también efectos sobre la salud pública. Road Dust (RD), traducible como el polvo de las carreteras, (o también polvo vial), y sus contaminantes adsorbidos han sido considerados como una de las fuentes principales de contaminantes que se difunden en las aguas pluviales. De ahí la necesidad de reconocer los tipos, las concentraciones y la distribución de contaminantes asociados, a fin de poder establecer estrategias de mitigación adecuadas.

SUMMARY

The urban environments of Latin America's medium-sized cities are home to more than 85% of its population; such accelerated urbanisation, multiple commercial activities and high traffic flow rates have led to increased urban environmental pollution, roads having become reservoirs of inorganic pollutants, such as those called potentially toxic elements (PTE), including heavy metals. Whilst such concentration of elements constitutes a risk factor for public health, it also affects natural resources providing significant ecosystem services, such as soil and water.

Problems related to PTE accumulation tend to become heightened, given the tendency for populations to increase and this type of city's dynamics directly affecting such increase, linked to a lack of real urban planning. An example of such lack of planning can be found in the lack of treatment for rainwater transporting pollutants to peri-urban areas, especially affecting their agricultural soils by changing their physical-chemical condition.

A series of studies has been carried out during the last two decades in response to this problem, aimed at investigating PTE concentrations and distribution patterns in soils/sediments or road dust (RD), as well as the related ecological and health risks. The city of Villavicencio, a medium-sized city having around 500,000 inhabitants in 2017, has been considered one of the fastest growing Colombian cities in recent years because, as points of entry to and exit from the Orinoquia region are concentrated here, it meets the parameters for new economic geography regarding the country's energy, agro-industrial and mining sectors. In view of the forgoing, a study was carried out for analysing the heavy metals in RD from Villavicencio's urban area and their possible effects on peri-urban agricultural land. The concentration and spatial distribution of five heavy metals (i.e. lead (Pb), chromium (Cr), cadmium (Cd), zinc (Zn) and copper (Cu)) were thus identified and evaluated, since they are considered the most problematic worldwide. Atomic absorption spectrophotometry (AAS) was used for analysing them in RD from Villavicencio's urban areas, starting from the premise of dividing the city's land coverage/territory into sub-areas, according to differing land use. Additionally, a risk analysis was carried out.

Given that agricultural use partially accounts for Villavicencio's peri-urban area, it was considered convenient to address recognition of these heavy metals in soils subjected to such use, since such metals in urban dust might migrate through the rainwater to agricultural soils. Soil samples were then taken for analysis in the laboratory regarding the content of such elements and characteristics of agronomic interest were determined in such soils.

Regarding RD from three areas of the city having differing functional activities (residential, commercial and roads), it was seen that average heavy metal concentrations (in mg/kg) followed the following sequences. The results for the commercial sector gave 1,289.4 Pb, 490.2 Cu, 387.6 Zn, 60.2 Cr and 54.3 Ni, the road sector had 133.3 Zn, 126.3 Cu, 87.5 Pb, 9.4 Cr and 5.3 Ni and the residential sector had 108.3 Zn, 26.0 Pb, 23.7 Cu, 7.3 Cr and 7.2 Ni.

The geoaccumulation index (I-geo) was used for discriminating the values so obtained; it was thus deduced that the commercial sector was heavily contaminated, whilst the two other sectors fell into the uncontaminated category. The ecological risk index similarly placed the commercial sector in the greatest risk category, while the other sectors were classified as low risk. Risk levels were not reached in human health risk analysis. The Kruskal-Wallis H test suggested that the type of land use had a significant influence on the metals' spatial variation; two potential sources were thus identified: one based on geochemical origin and the other on vehicle-related activity.

Analysis of peri-urban agricultural land irrigated with river water, potentially contaminated by the city's storm-water runoff gave heavy metal concentrations below quantification limits, meaning that they were not contaminated. No physicochemical alterations were found regarding agricultural fields' properties (i.e. there was no evidence of a change or effect from heavy metal contributions). This could have been associated with climatic factors (temperature and rainfall) contributing to the rapid degradation of organic matter (which was almost absent in samples), meaning that its nutrient and heavy metal retention function was insignificant/null. Heavy rain (more than 3,000 mm/year) has an enormous capacity for exporting heavy metals, although plants would absorb some.

The data reported here could facilitate identifying heavy metal contamination hot spots in urban areas; such information can provide a crucial tool for urban planning and environmental management. Evan though no substantial changes were found in Villavicencio's peri-urban areas' agricultural soils, a follow-up and monitoring scheme must be maintained for control purposes and thus enable early decisions to be taken guaranteeing resource conservation whilst avoiding effects on public health. RD (meaning both road dust and its adsorbed pollutants) has been considered one of the main sources of pollutants spread by rainwater. There is thus a need to recognise associated pollutants' types, concentrations and distribution to establish suitable mitigation strategies.

ÍNDICE GENERAL

ÍNDICE DE TABLAS

ÍNDICE DE FIGURAS

ÍNDICE DE ABREVIATURAS

CR	Nivel de riesgo de cáncer	Cancer risk level
CSF	Factor pendiente	Slope factor
GIS	Sistema de Información geográfica	Geographic information system
GP	Parques públicos	Public parks
HCA	Análisis jerárquico cluster	Hierarchical cluster analysis
HI	Índice de peligro	Hazard index
HQ	Cociente de peligro	Hazard quotient
I-geo	ïndice de geoacumulación	Geo-accumulation index
LAC	América y el Caribe	America and the Caribbean
LADD	Efecto carcinogénico	Carcinogenic effect
MDL	Límite de detección del método	Method's detection limit
OM	Materia orgánica	Organic matter
PCA	Análisis en componentes principales	Principal component analyse
PLI	Índice de carga contaminante	Pollution Load Index
RDS	Sedimento depositado en carretera	Road-deposited sediment
RfD	Dosis de referencia	Reference Dose
RfD_{dermal}	Dosis de referencia dérmico	Dermal reference dose
RfD_{ing}	Dosis de referencia de ingestión	Ingestion reference dose
RfD_{inh}	Dosis de referencia de inhalación	Inhalation reference dose
RI	Riesgo ecológico	Ecological risk
SD	Desviación estándar	Standard deviation
USEPA	Agencia de Protección USA	United States Environmental Protection Agency

1. INTRODUCCIÓN

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El crecimiento poblacional, las actividades industriales y comerciales, el alto flujo vehicular, el material de pavimentación de vías y los aportes atmosféricos son las principales causas de la contaminación ambiental urbana (Saeedi, *et al*., 2012; Zafra *et al*., 2013), donde hay presencia de metales pesados que constituyen algunos factores de riesgo para la salud pública y para los sistemas naturales que integran las ciudades (Fergusson y Ryan, 1984; Lui *et al*., 2014). La ciudad de Villavicencio, por su ubicación geográfica cumple un rol fundamental en la dinámica económica del país, debido a que es un punto de conexión por donde se movilizan tanto productos alimentarios, como hidrocarburos procedentes de los Llanos Orientales al centro del país. A la par se ha generado un crecimiento urbanístico acelerado, un aumento en el parque automotor, y una mayor oferta y demanda de bienes y servicios, que aumentan los riesgos de contaminación urbana.

La dinámica social y económica de las ciudades, el modelo de crecimiento y el diseño basado en la preferencia del uso del vehículo privado sobre el público como modo de desplazamiento, al igual que la desarticulación de lo urbano y lo rural, han contribuido al aumento de un problema propio, la congestión del transporte de población y de carga (Montezuma, 2003), que ha conducido a presiones sobre su entorno y al incremento constante en la demanda de servicios y generación permanente de residuos (Murakami *et al*., 2005). Esta sobrecarga en la movilidad sumada a factores como emisiones industriales y en general a la dinámica económica del área, ha convertido a las vías en importantes receptores de contaminantes que constituyen potenciales problemas para la salud pública de los usuarios de las vías, de los habitantes aledaños y de la dinámica ecológica de los sistemas naturales (Bris *et al*., 1999; Useche Y Wahab, 2005; Brown Y Peake, 2006; Bae *et al*., 2006; Aelion *et al*., 2009; Zafra *et al*., 2013).

En este sentido, es importante destacar el papel de los vehículos como principales fuentes de elementos contaminantes en las vías, tales como metales pesados que pueden provenir de los tubos de escape o exostos, de los aceites lubricantes, de los combustibles utilizados gasolina o diesel, del desgaste de frenos, de las partículas de neumáticos, entre otros (Adachi y Tainoshob, 2004; Zafra-Mejía *et al*., 2013). Davis y Birch (2010), argumentan que en las cuencas urbanizadas, las vías pueden constituir un 22% del área y éstas contribuyen con el 26% de la escorrentía. Por otro lado, Sartor *et al*. (1974), determinaron que la carga de contaminantes de las aguas de escorrentía urbana es significativamente mayor en comparación con la escorrentía rural. Esto determina, que gran parte de la contaminación de las fuentes hídricas urbanas y de los suelos aledaños (Hewitt y Rashed, 1991), estén relacionadas con los aportes viales (Vaze y Chiew, 2002). Rissler *et al*., 2012, encontraron que los principales contaminantes asociados a las cuencas urbanizadas son el Cobre (Cu), el Plomo (Pb) y el Zinc (Zn), que hacen parte del grupo de los metales pesados.

A nivel mundial, se han realizado investigaciones orientadas a detectar la presencia de metales pesados en el polvo vial de diferentes ciudades, ya que éste se constituye en el principal sumidero de contaminantes como los metales pesados, donde el contacto y la ingestión de partículas provenientes de éstos pueden traer graves problemas para la salud humana (Zheng *et al*., 2010; Acosta *et al*., 2014). Basados en lo anterior, el monitoreo de vías que presentan alto flujo vehicular y que además hacen pates de zonas industriales, se han convertido en una tarea prioritaria de los programas de salud pública y de gestión del riesgo (Nazzal *et al*., 2012). En la tabla 1.1, se presentan los resultados de metales pesados presentes en el polvo vial de estudios realizados en países de diferentes continentes como: China (Yekeen y Onifade, 2012), Egipto (Khairy *et al*., 2011), Nigeria (Abdel-Latif y Saleh, 2012), Irán (Saeedi *et al.,* 2012), Ghana (Atiemo *et al*., 2011), España (Acosta *et al.,* 2014). En estudios particulares como los de Palermo (Italia) y Sídney (Australia) las concentraciones de Pb encontradas fueron del orden de 544 y 511 mg/Kg respectivamente. En el caso de Murcia en España, se detectó que las mayores concentraciones de Pb están asociadas al sector industrial con 346 mg/Kg, mientras que en el sector residencial fue de 123 mg/Kg.

Table 1.1 Concentración de metales pesados en polvo vial de ciudades en el mundo

Metales pesados (mg/kg)*								**Zona**	**Localidad**	**Autor**
Cd	**Cu**	**Pb**	**Cr**	**Ni**	**Zn**	**Fe**	**Mn**			
10,7	225,3	257,4	33,4	34,8	873,2	47935,7	1214,5	Ciudad	Tehran	Saeedi *et a*l. (2012)
0,8	-	234,6	36,9	25,4	634,4	-	-	Ciudad	Cairo	Abdel-Latif y Saleh (2012)
-	29,0	33,6	123,8	9,3	124,5	19782,0	275,4	Vía John Teye Pokuase	Ghana	Atiemo *et al.* (2011)
-	48,3	58,7	166,8	15,9	161,4	23786,3	235,9	Vía Mallam Junction Weija		
-	43,5	117,5	152,3	6,5	213,3	35871,9	355,8	Autopista Tema Motorway		
-	76,5	92,3	220,4	13,4	371,7	36630,3	379,6	Tetteh Quarshie		
0,6	72,1	201,8	69,3	26,0	219,2	-	-	Ciudad	Beijing	Du *et a*l. (2013)
1,1	98,0	544,0	218,0	14,0	207,0	-	-	Ciudad	Palermo	Varrica *et al,* (2003)
0,4	65,8	39,1	43,3	15,1	112,5	-	-	Ciudad	Ottawa	Rasmussen *et al,* (2001)
2,6	91,8	346,0	-	-	315,0	-	-	Industrial Suroeste	Murcia	Acosta *et al.* (2014)
4,6	80,9	117,0	-	-	147,0	-	-	Industrial Noroeste		
0,7	130,0	123,0	-	-	377,0	-		Residencial		
-	124,3	511,0	19,3	-	248,6	13259,6	-	Universidad Nueva Gales del Sur	Sydney	Ball et al. (1998)

Investigaciones realizadas en España y Noruega determinaron mediante análisis de componentes principales y clúster, que la presencia de metales pesados en polvo de carretera está relacionada con el tipo de automotores, flujos vehiculares, construcción de edificios y con las fuentes naturales (De Miguel *et al.,* 1997). Por otro lado, se relaciona la presencia de Pb, Cu, cadmio (Cd) y Zn con el uso de combustibles fósiles, desgaste de neumáticos y pastillas de frenos, aceites, de lubricantes y grasas (Christoforidis y Stamatis, 2009), mientras que cromo (Cr) y el níquel (Ni) tiene como fuente principal el desgaste de partes metálicas y accesorios cromados (Al-Shayep y Seaward, 2001).

El polvo vial es una mezcla compleja de partículas y puede contener varios componentes como sustancias orgánicas, metales pesados, otros inorgánicos, esporas de moho, caspa de animales, polen, fragmentos de polen, etc., que posiblemente pueden resuspenderse debido al movimiento de los vehículos y el viento, dando como resultado una importante fuente de contaminación atmosférica del aire. Se observó que las partículas y los metales asociados, particularmente con polvo fino, permanecen suspendidos en el aire por más tiempo bajo ciertas condiciones meteorológicas. El polvo de carretera, es un importante indicador ambiental de la contaminación por metales proveniente de la deposición atmosférica, recibe diversos insumos de metales antropogénicos de diversas fuentes estacionarias y móviles, como el tráfico vehicular, actividades industriales, centrales eléctricas, quema de combustibles fósiles residenciales, incineración de desechos, construcción y demolición y resuspensión de suelo contaminado (Bilos et al., 2001; Charlesworth et al., 2003; Bhanarkar et al., 2005, 2008; Gupta et al., 2012).

En Colombia los estudios relacionados con metales pesados han sido enfocados hacia los sedimentos acuáticos continentales y marinos, mientras que para el polvo vial aún son muy escasos. Con referencia a ciudades, se destaca los estudios realizados por Zafra y colaboradores, para el caso del municipio de Soacha – Cundinamarca, donde abordan el tamaño de partícula de carretera, identificando que las mayores concentraciones metálicas están asociadas a tamaños de partícula menores de 63 μm (Zafra *et al*., 2013). Así mismo, señalan que los metales acumulados más destacados en el corredor vial del municipio son el Pb y el Zn, los cuales deben tener mayor interés por parte de las autoridades de control (Zafra *et al*., 2013). En el estudio sobre la asociación de los metales con el polvo atmosférico determinaron que el Pb estaba en una concentración 17,6 veces mayor en PM10 que en lo encontrado en los sedimentos viales (Zafra *et al.,* 2013). Finalmente en el análisis de los sedimentos con los procesos de escorrentía concluye que en los periodos secos la acumulación de metales pesados en el polvo vial es mayor y que en la medida que el tamaño de las partículas de éstos sean menores, existe mayor probabilidad que sean arrastrados por la escorrentía urbana (Zafra *et al*., 2009).

En sí, el polvo de carreta y sus contaminantes adsorbidos se consideran como una de las principales fuentes de contaminación difusa de las aguas pluviales (Loganathan et al. 2013; Zhao et al. 2018). No resulta extraño por tanto, que en la Directiva europea (en su última actualización del 8 de junio de 2016), se señale la necesidad de identificar y cuantificar las fuentes de contaminación difusa ligadas al polvo de carretera, para establecer criterios acerca de la necesidad de mitigar la escorrentía superficial por contaminación acuática inducida. Particular atención merece los contaminantes adsorbidos en cuanto que potenciales contaminantes que se pueden movilizar en forma difusa a través dela escorrentía de aguas pluviales.

1.1. Características de los metales pesados

Los elementos metálicos se distinguen de los demás elementos de la tabla periódica debido a sus propiedades físicas como la conducción de calor, ductilidad y maleabilidad, resistencia eléctrica, presencia brillo y que no son degradados a través de procesos bilógicos (Housecroft y Sharpe 2008). Del mismo modo, Duffus (2002), plantea que los metales pesados tienen densidad superior a 6 g/cm^3 y que el término “metal pesado” se ha utilizado para referirse a los que pueden causar daño ambiental. En la tabla 1.2, se presentan algunas características generales de los metales pesados y las concentraciones globales promedio en suelos. Por otro lado, el factor toxicológico ha sido fundamental en la definición de estos elementos; sin embargo, en este aspecto es necesario considerar la relación dosis-respuesta, donde algunos iones metálicos son determinantes en el metabolismo celular en bajas concentraciones, pero son tóxicos en concentraciones mayores, entre ellos figuran el Cromo (Cr), Cobre Cu, Hierro (Fe), Manganeso (Mn), Molibdeno (Mo), Ni Zn (Appenroth, 2010). Otros elementos como Plomo (Pb), Mercurio (Hg), Cadmio (Cd) y Arsénico (As) aún en pequeñas concentraciones son altamente tóxicos, siendo promotores de enfermedades como el cáncer (Willers *et al*., 2005, Micó *et al.,* 2007).

Table 1.2. Características generales de los metales pesados

Metal	Densidad (g/Cm^3)	Nº Atómico	Suelos (mg/Kg)	Esencial	Tóxico
Cd	8,7	48	0,35	-	A, P, H
Co	8,9	27	8	A, P, H	A, P, H
Cr	7,2	24	40	A, H	P, H
Cu	8,9	29	30	A, P, H	P
Fe	7,9	26	25×10^3	A, P, H	H
Mn	7,4	25	1000	A, P, H	P
Ni	8,9	28	20	A, P, H	A, P, H
Pb	11,3	82	29	-	A, P, H
Zn	7,1	30	90	A, P, H	P

A, Animales; P, Plantas; H, Humanos.
Fuente: Mico *et al*. (2005)

Los metales pesados pueden tener origen natural cuando proviene de material parental, o antrópico cuando la fuente son actividades desarrolladas por el hombre (Micó *et al*,. 2007). Estas fuentes antrópicas están asociadas con diferentes actividades como la urbana-industrial, la minería, la agrícola y las relacionadas con la movilidad, tales como vehículos, las vías y los centros de servicio mecánico. En la tabla 1.3, se presenta un listado de partes y lubricantes de vehículos y los metales pesados con los que se asocian (Zafra *et al.,* 2013; Jiménez Ballesta 2017).

En el caso del polvo de carretera los metales presentes pueden transferirse al hombre a través de la inhalación, de la ingestión y de la vía dérmica, cuando se levantan a la atmosfera por acción del viento o turbulencia causada por los vehículos. Los efectos toxicológicos de los metales hacia los humanos, particularmente de Cd, Zn, Hg y Pb, son los más documentados por ser los más peligrosos.

1.1.1. Plomo (Pb)

Desde los romanos se han reconocido los efectos tóxicos del Pb, debido a que era utilizado como revestimiento en sus acueductos (Meyer *et al*., 2008). Actualmente existe mayor control para su uso industrial y en los combustibles han disminuido sus concentraciones, sin embargo, la contaminación por Pb aún hace parte de los problemas que afronta la salud pública en regiones como áfrica, Asia y Latino-América (Meyer *et al*., 2008; Sabath, y Robles-Osorio, 2012).

El plomo forma parte del grupo de los metales no esenciales, y los niveles de atención en humanos es de 10µg/dL en niños, de 25µg/dL en adultos y para mujeres embarazadas de 5 µg/dL; en animales la toxicidad está alrededor de 30 mg por kg en la dieta. Una vez introducido en el organismo el Pb se distribuye de forma sistémica, se une a la membrana y hemoglobina de los eritrocitos, fijándose en cerebro, riñón, hígado, músculos y tejido óseo. Interacciona con metales esenciales como Fe, Ca, Zn, Cu y compite con estos y/o modifica sus concentraciones. Desde el punto de vista fisiológico inhibe el ATP_{asa} sódico-potásico y demás enzimas respiratorias. Los efectos de salud a nivel humano que más se destacan son: anemia hemolítica, neuropatías y encefalopatías (Charris *et* al., 2011).

Table 1.3 Estructuras y lubricantes de vehículos asociados con metales pesados

Metal	**FUENTE**						
	Pastillas de frenos	**Escape**	**Neumáticos**	**Aceite, grasa y lubricantes**	**Partes móviles**	**Cojinetes y rodamientos**	**Recubrimiento metálico**
Plomo -Pb	X	X	X	X	X	X	
Cinc -Zn	X		X	X			
Hierro -Fe	X				X		
Cadmio -Cd	X	X	X	X			
Cromo -Cr	X				X		X
Cobre -Cu	X		X	X	X	X	X
Níquel -Ni	X	X		X	X		X

1.1.2. Cadmio (Cd)

Es un metal ampliamente representado en los ambientes terrestres y acuáticos, pero en concentraciones relativamente bajas; las erupciones volcánicas son su principal fuente natural, mientras que la quema de residuos, la producción de hierro y acero, y la combustión de combustibles fósiles se destacan como sus principales fuentes antrópicas (WHO, 2007). Como mineral se encuentra bajo la forma de sulfuro de cadmio asociado casi siempre con el Zn, asociación potencialmente peligrosa debido a que el Zn es un elemento esencial para los sistemas biológicos (Ziemacki *et al.,* 1989).

La absorción principalmente es por inhalación mediante las vías respiratorias y a través la dermis, sin embargo aún no se registran casos de intoxicación en las fuentes de información de salud pública. El Cd puede permanecer en el organismo por tiempo superior a 20 años, fijándose en el sistema renal (Sabath, y Robles-Osorio, 2012). Inhibe los sistemas enzimáticos y es antagonista del Zn, altera la formación de ácidos nucleicos y proteínas, la máxima dosis diaria referencial en la dieta humana es de 70 mg/Kg (WHO, 2007). La concentración crítica que produce daño de la corteza renal es de 200 mg/Kg. Los síntomas de intoxicación pueden ser agudos como irritación del tracto digestivo, cefalea, escalofrío, parálisis y depresión cardiovascular, y los crónicos producen lesiones óseas y renales (Sabath, y Robles-Osorio, 2012).

1.1.3. Hierro (Fe)

Esencial en los seres vivos, hace parte de la molécula de la hemoglobina y de tejidos, tiene funciones como cofactor de enzimas, además juega un papel fundamental en los mecanismos de respuesta inmune y su deficiencia genera anemia ferropenia. Es un metal potencialmente tóxico en todos sus estados de oxidación, su exceso puede producir patologías gastrointestinales, cardiovasculares y neurológicas (Guerra *et al*., 2012).

1.1.4. Zinc (Zn)

Es un Elemento con amplia distribución, sin embargo únicamente representa el 0,00125% de la corteza terrestre, y parte del Zn que se procesa termina en la industria automotor (González-Reimers *et al.,* 1998). En los seres vivos es el segundo oligoelemento de mayor abundancia después del hierro; su deficiencia en los seres humanos puede causar retraso en el crecimiento y en el desarrollo neuronal, diarrea y alteraciones inmunitarias (Barceloux, 1999). La deficiencia puede provocar, entre otros, baja tasa de crecimiento, alteraciones mentales, alteraciones en la forma y función de los órganos reproductores masculinos, alteraciones en el sentido del gusto y olfato, depresión inmunitaria, baja tolerancia a la glucosa. Es un metal de baja toxicidad, sin embargo cuando se ingieren cantidades, superiores a 150 mg/Kg, puede generar intoxicación con síntomas como nauseas, vómitos y fiebre, y se asocia a enfermedades como el cáncer de próstata y alteraciones en el sistema inmune (Rubio *et al*., 2007).

1.1.5. Cobre (Cu)

Este elemento hace parte de los sistemas enzimáticos, principalmente de los invertebrados, en los seres humanos está ligado a la albumina y su toxicidad se relaciona con la aparición de toxinas microbianas; en años anteriores la utilización de recipientes de cocina mal estañados era la principal fuente de intoxicación. La toxicidad en ganado vacuno y ovejas se presenta en niveles entre 25 a 100 mg/Kg y en plantas la dosis tóxica fluctúa entre 5 a 40 mg/Kg (González-Reimers *et al*., 1998).

1.1.6. Cromo (Cr)

Tiene amplia utilización en la industria y los combustibles fósiles contienen altas concentraciones, de ahí las cantidades que se liberan en la combustión de los automotores. Los compuestos que forma el cromo se consideran entre los más contaminantes desde el punto de vista ambiental, pues pueden ser causantes de reacciones carcinógenas y mutagénicas. El Cr^{+3} es esencial, juega un papel importante en el metabolismo de la glucosa, actuando como cofactor de la insulina, y su carencia se asocia a la diabetes y a enfermedades cardiovasculares en la madurez, pero en el estado Cr^{+6} puede generar cáncer de pulmón (Ziemacki *et al.,* 1989).

1.1.7. Níquel (Ni)

Es un oligoelemento que se encuentra en la corteza terrestre en una concentración media de 75 mg/kg (Ziemacki *et al.,* 1989). Este elemento es esencial para animales y plantas, pero es de menor importancia para el hombre. En el suelo participa en la fijación de nitrógeno, su déficit puede limitar la actividad de *Rhizobium* spp (Malavolta y Moraes, 2007). Las principales rutas para adquirir el Ni son las vías oral dérmica y respiratoria, y entre las consecuencias por intoxicación esta la interacción con las membranas lipídicas y la alteración de macromoléculas, la concentración tóxica en animales está entre 500 y 100 gr/Kg (Lozano, 2009).

1.2. Relevancia y objetivos del presente estudio

Los procesos de crecimiento urbano en ciudades especialmente de los países en vía de desarrollo se resaltan por la carencia de planeación urbana, así como en la oferta irregular de los servicios de saneamiento, falencias en los servicios de transporte de mercancías y pasajeros, y segregación social; factores relacionados con los procesos de deterioro de los recursos naturales de su territorio.

La ciudad Villavicencio, es considerada por el Banco Interamericano de Desarrollo (www.iadb.org, 2014), de tipo emergente, que presenta características como la poca planeación urbana, especialmente en lo concerniente a los sistemas de tratamientos de aguas residuales y lluvias, importantes para este estudio, debido que son las que lavan las vías y entregan grandes cantidades de contaminantes a las fuentes naturales aumentando el riesgo ecológico, en Villavicencio presenta un régimen lluvioso alto en cuanto al número de días, que de acuerdo con reportes del IDEAM alcanza un promedio de 223 días en el año.

Este tipo de estudio debe ser abordado en numerosas ciudades colombianas, como es el caso de Villavicencio, especialmente si, como sucede con esta ciudad, queda ubicada en un punto estratégico de paso obligado para la comunicación y el transporte terrestre de mercancías desde los Llanos Orientales hacia el centro del país. En efecto, se destaca que por sus vías se movilizan carro-cisternas para el transporte de petróleo y productos oleaginosos, de buses intermunicipales de pasajeros, de camiones de diferente tonelaje con alimentos agropecuarios y demás vehículos públicos y privados. Otro factor importante a tener en cuenta, es la dinámica en la construcción de viviendas y avenidas que para el año de 2011 alcanzó un crecimiento de 23,67%, superior a ciudades como Bogotá, Medellín o Barranquilla (Alcaldía de Villavicencio, 2013).

De acuerdo con lo anterior, dada la escasa información existente en Colombia y en particular en Villavicencio sobre la acumulación de metales pesados en polvo vial, en la presente tesis doctoral se aborda la evaluación de sus contenidos y su distribución espacial en el área urbana de la ciudad a partir de las concentraciones de metales pesados presentes en dicho polvo vial; adicionalmente se valoran los riesgos que representan. Finalmente se investiga el posible efecto del riego con aguas potencialmente contaminadas sobre suelos periurbanos dedicados a uso agrícola.

Como corolario de esta tesis, se espera que la información obtenida suponga un criterio para que las autoridades ambientales locales generen estrategias de gestión ambiental que permitan mitigar y controlar los problemas ocasionados por los metales pesados derivados de las zonas viales de las ciudades como es el caso de Villavicencio.

En concreto los objetivos planteados son los siguientes:

• Analizar los niveles de algunos metales pesados (Cu, Pb, Ni, Zn, Cd y Cr) en polvo vial del espacio urbano que ocupa la ciudad de Villavicencio (Colombia), con énfasis en los diferentes tipos de zonas que conforman la ciudad.

• Investigar las diferencias entre los valores encontrados y los de referencia.

• Determinar la distribución espacial de los citados metales pesados, evaluando el efecto de los diferentes usos dentro de la ciudad.

• Aplicar índices de contaminación y de riesgo a la salud humana para diagnosticar posible contaminación, de tal modo que se pueda disponer de una herramienta a la hora de la toma de decisiones.

• Evaluar el efecto sobre las propiedades del suelo irrigado con aguas contaminadas provenientes tanto de polvo vial como de fuentes domésticas e industriales, que permita establecer acciones con el ánimo de preservar la salud pública y los recursos naturales.

1.3. Publicaciones derivadas de la Tesis

Durante el desarrollo de este trabajo de investigación se publicaron tres artículos científicos en revistas internacionales con índice de impacto.

Trujillo-González, J. M., Torres-Mora, M. A., Keesstra, S., Brevik, E. C., & Jiménez-Ballesta, R. (2016). Heavy metal accumulation related to population density in road dust samples taken from urban sites under different land uses. Science of the Total Environment, 553, 636-642. doi: https://doi.org/10.1016/j.scitotenv.2016.02.101

Trujillo-González, J. M., Torres-Mora, M. A., Jiménez-Ballesta, R. & Zhang, J. (2018). Land-use-dependent spatial variation and exposure risk of heavy metals in road-deposited sediment in Villavicencio, Colombia. Environmental Geochemistry and Health. https://doi.org/10.1007/s10653-018-0160-6

Trujillo-González, J. M., Mahecha-Pulido, J. D., Torres-Mora, M. A., Brevik, E. C., Keesstra, S. D., & Jiménez-Ballesta, R. (2017). Impact of Potentially Contaminated River Water on Agricultural Irrigated Soils in an Equatorial Climate. Agriculture, 7(7), 52. doi: https://doi.org/10.3390/agriculture7070052

No se incluyen otros trabajos publicados en revistas de menor impacto y en los Proceedings de congresos nacionales e internacionales.

2. ÁREA DE ESTUDIO

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EL municipio de Villavicencio, capital del Departamento de Meta, está localizado, en el centro oriente de Colombia, en la margen derecha del río Guatiquía a los 4º 09' 12" de latitud norte y 73º 39' 06" de longitud oeste, con una altura media de 467 metros sobre el nivel del mar (Figura 2.1). Villavicencio es la ciudad más importante de los Llanos orientales colombianos. El área del municipio alcanza los 1.262 Km^2 y está limitada al norte por los municipios de Restrepo y el Calvario, al oriente por Puerto López, al sur por San Carlos de Guaroa y Acacias, y al occidente por el municipio de Acacias y el Departamento de Cundinamarca. Se encuentra a 126 kilómetros de Bogotá, capital de Colombia, y cuenta con una población aproximada para el año 2017, según proyecciones del Departamento Administrativo Nacional de Estadística de 500 000 habitantes (DANE, 2010).

Fisiográficamente, el municipio presenta dos grandes unidades, la plana o de llanura y la vertiente de la cordillera que incluye el Piedemonte. En la primera se identifican planicies aluviales y terrazas aluviales con diferentes elevaciones y valles (25% del territorio). La vertiente de la cordillera se puede dividir en pie de vertiente con los abanicos fluvioterrenciales, laderas irregulares muy disectadas y colinas (75% del territorio) (Figura 2.2; 2.3).

Geológicamente, el municipio se encuentra en la vertiente de la cordillera oriental que está constituida por materiales metamórficos (esquistos) en forma de inclusiones entre lutitas y areniscas cretácicas. En la parte baja se encuentran depósitos terciarios y cuaternarios; estos últimos forman parte de abanicos aluvio-coluviales, coluviones, terrazas fluviales, y depósitos aluviales recientes (Goosen 1964) (Tabla 2.1).

Tabla 2.1 Zonas geomorfológicas del municipio de Villavicencio.

Provincia fisiográfica	Unidad Climática	Gran Paisaje	Paisaje	Subpaisaje	Simbolo
Vertiente oriental de la cordillera oriental	Cálido húmedo	Relieve montañoso denudativo	Montañas erosionales en rocas sedimentarias	Laderas erosionales en pendiente de fuertemente quebradas a escarpadas	Ch111
			Vallecitos intramontanos	Plano de inundación	Ch121
Megacuenca de sedimentación de la Orinoquia	Cálido húmedo	Planicie aluvial de desborde	Plano de inundación.	Complejo de orillares	Ch211
				Vega baja	Ch212
			Sobrevega		Ch221
			Terraza		Ch321
		Piedemonte aluvial	Abanico	Superficie no disectada	Ch311

Los procesos morfodinámicos pueden agruparse en dos grandes unidades: procesos erosivos y procesos de sedimentación. Los primeros se presentan en las vertientes de la cordillera (zona alta de las cuencas de los ríos Guatiquía y Guayuriba) y en la parte alta de las microcuencas del piedemonte y los segundos en la zona de la llanura.

Las rocas próximas a la ciudad de Villavicencio se encuentran fuertemente plegadas y falladas a partir del levantamiento de la cordillera oriental durante el Mio-plioceno (Caballero et al., 2010). El área de las colinas próximas que se localizan en la parte media y alta de la microcuencas de los caños Parrado, Gramalote, Maizaro, La Argentina y Buque, se encuentran sumamente fracturadas debido a dos fallas principales del sistema del Piedemonte Llanero; la falla de Servitá-Restrepo y la falla de Mirador-Restrepo con actividad neotectónica (Caballero et al., 2010; Chavez-Narváez y González-Pérez, 2018) (Figura 2.4, 2.5). De todas estas zonas, en la que se lleva a cabo el trabajo presente es fundamentalmente Llanura aluvial (donde se sitúa la ciudad) mientras que los suelos dedicados a cultivo en la zona periurbana son aluviones recientes.

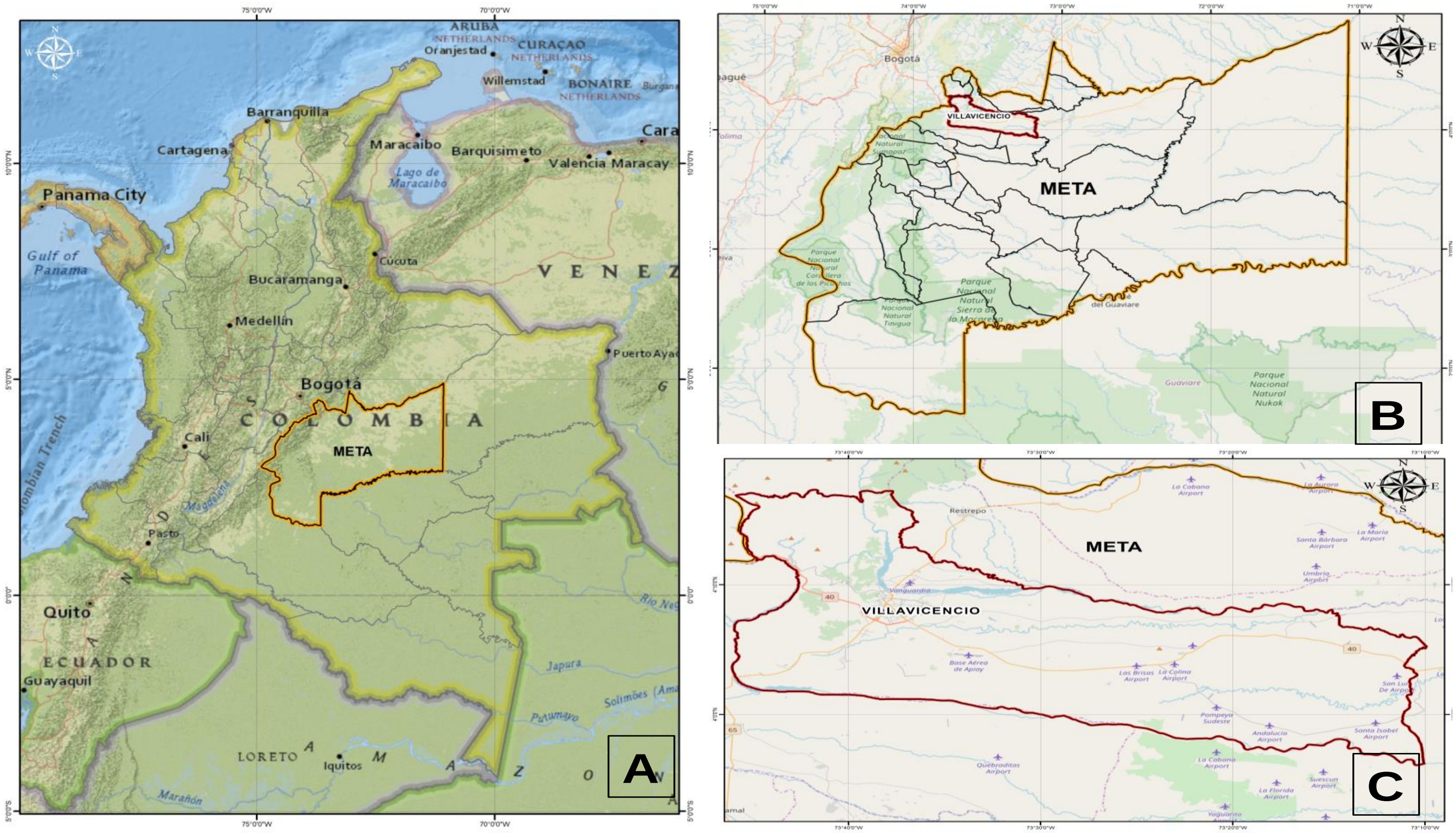

Figura 2.1 Ubicación geográfica de Villavicencio, Colombia. A) Colombia. B) Departamento de Meta. C) Municipio de Villavicencio

Figura 2.2 Fisiografía de Villavicencio. A) río Guatiquía y Villavicencio a su margen derecho. B) Río Guatiquía. C) Cordillera Oriental, Piedemonte del Llano colombiano

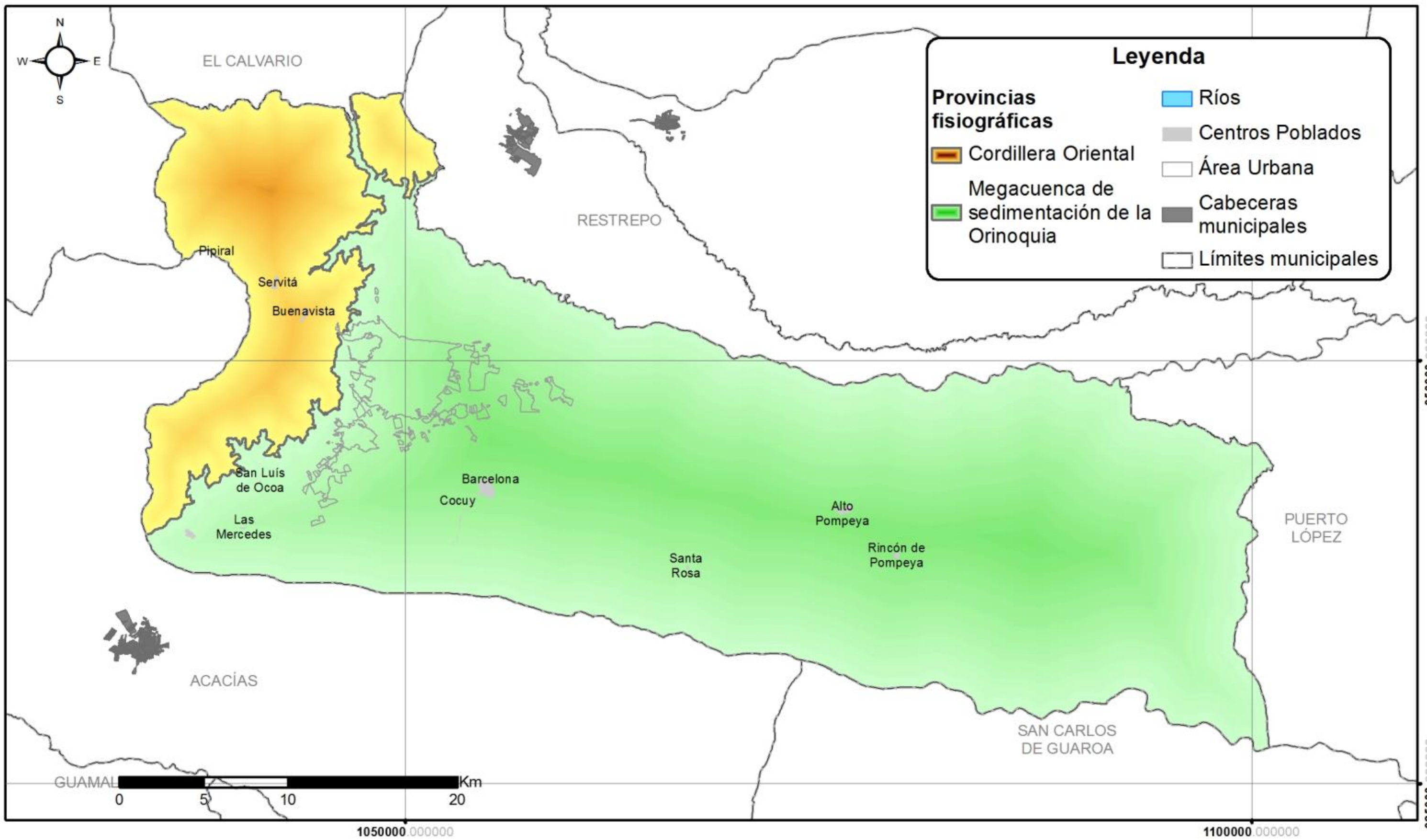

Figura 2.3 Provincias fisiográficas del municipio de Villavicencio, Colombia

Figura 2.4 Microcuenca del caño La Argentina

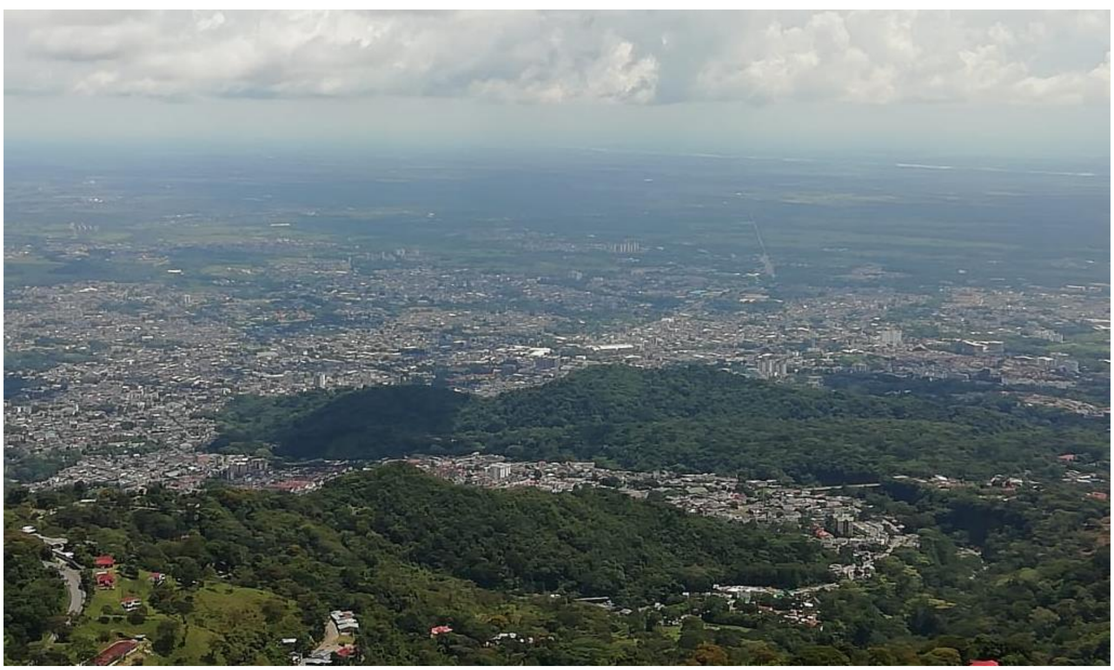

Figura 2.5 Ciudad de Villavicencio, vista desde la cordillera Oriental

Existe una intensa red hidrográfica observándose sobre las laderas, un patrón dendrítico a subdendrítico con muestras locales de control estructural, marcadamente radial sobre los abanicos Honda, Buque, Maizaro y Parrado y una dinámica de ríos trenzados y meándricos en la zona de llanura (Melo, 2018), Villavicencio queda limitado en tres costados por los ríos Guatiquía y Guayuriba en aproximadamente 130 km, Otras quebradas como Honda y el Guadual, Negra y salinas sirven igualmente de límite en longitud aproximadamente de 40 km. La cuenca del río Meta es la receptora de los afluentes del Municipio de Villavicencio y ésta vierte sus aguas a la gran cuenca del Orinoco.

En Villavicencio, los veranos son cortos, muy caliente y nublados y los inviernos son cortos, caliente, mojados y parcialmente nublados. Durante el transcurso del año, la temperatura generalmente varía de 20 °C *a* 32 °C y rara vez baja a menos de 16 °C o sube a más de 34 °C. El clima de Villavicencio según la clasificación climática de Koeppen es cálido húmedo tropical, caracterizado por fuerte pluviosidad, atemperado por un periodo verdaderamente seco. Se trata de un clima tropical estacional, estando la dinámica de la estacionalidad ligada a las oscilaciones en dirección N-S-N de la zona de convergencia intertropical (ZCIT) de poder climático. La temperatura promedio de la ciudad es de 27ºC (Figura 2.6), la humedad relativa es alto (80%) disminuyendo en los meses donde la temperatura aumenta (enero – Marzo) hasta 66%. Pero el dato climático más representativo son sus elevadas precipitaciones que, promedio alcanzan valores de hasta 4300 mm anuales (Figura 2.7). Sin embargo, Por su ubicación en el pie de la cordillera las lluvias cambian drásticamente en el territorio. La cordillera y el piedemonte se caracterizan por ser zonas de altas precipitaciones, la mayoría de origen orográfico. En la cuenca alta del río Guatiquía las mayores precipitaciones se presentan en las partes bajas de las microcuencas que no están al abrigo de los vientos. En las cabeceras de las subcuencas hidrográficas de los ríos Guatiquía y Guayuriba, se presenta un núcleo de precipitación máxima, en el cual se registra un total de precipitaciones promedio anual de 4000 mm/año (IDEAM, 2018. En la cuenca en la zona de la llanura, la precipitación varía de 2900 a 4000 mm, presentándose menores cantidades de lluvias hacia el Este del municipio (Figura 2.8).

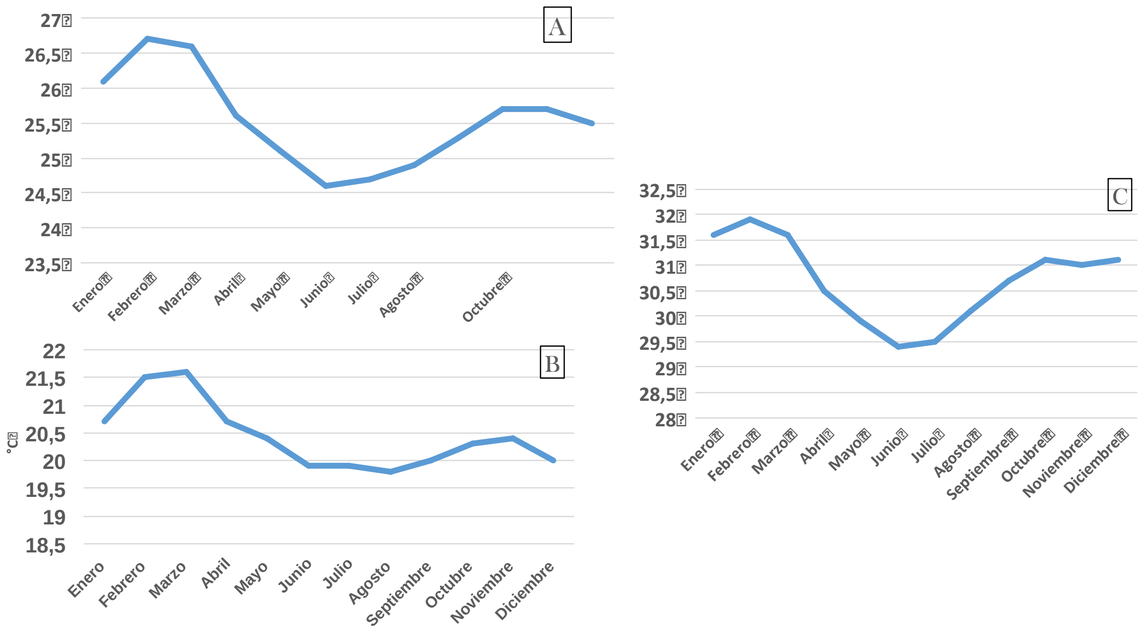

Figura 2.6 Variación temporal de la temperatura en Villavicencio. A) Temperatura media. B) Temperatura mínima. C) Temperatura Máxima.
Fuente: https://es.climate-data.org

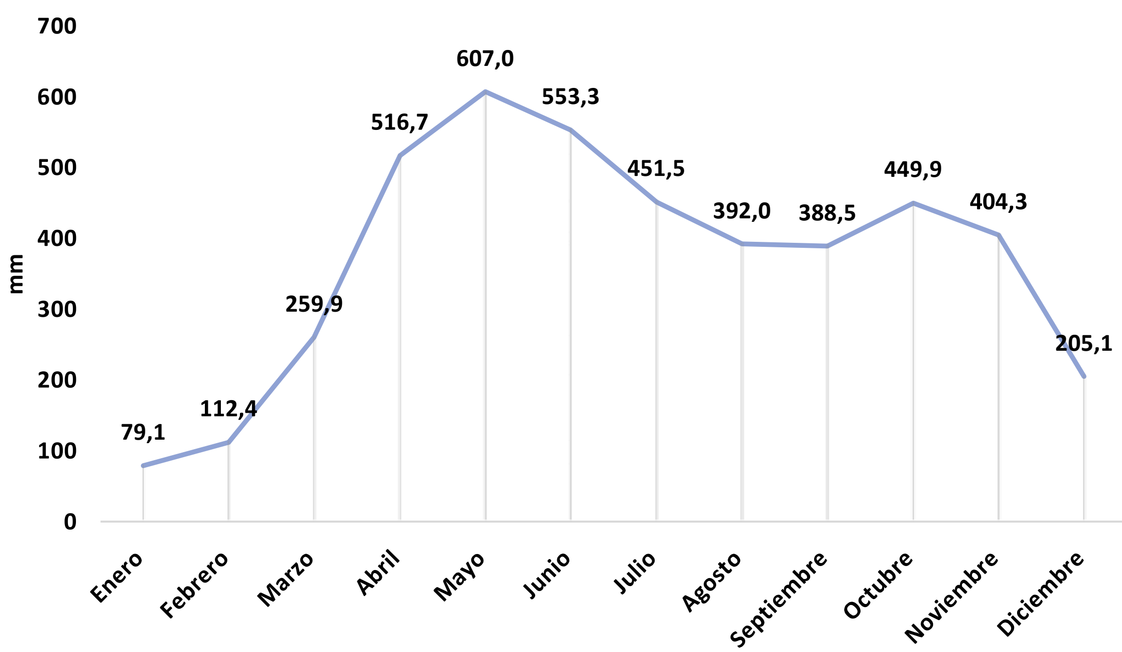

Figura 2.7 Precipitación promedio mensual de Villavicencio, Colombia (IDEAM)

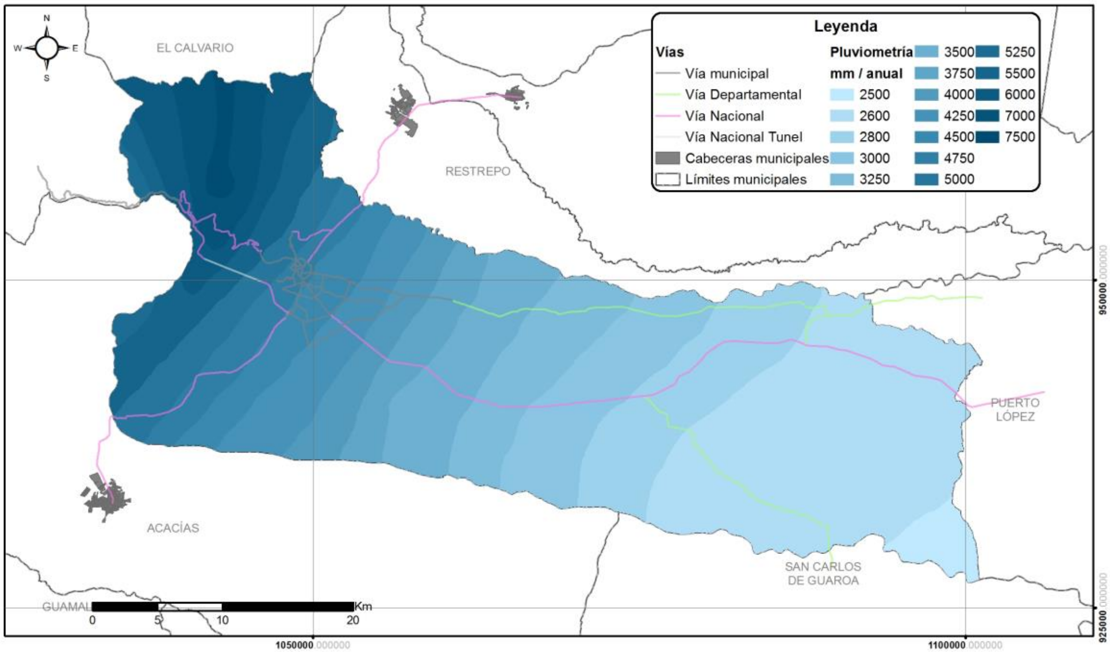

Figura 2.8 Distribución espacial de las precipitaciones en Villavicencio, Colombia
Fuente: POT (2015)

De acuerdo con la aptitud para la agricultura, los suelos del Departamento de Meta se identifican dentro de las 7 clases que van desde el más apto es decir aquel que ofrece altos rendimientos sin necesidad de insumos hasta el menos apto que se caracteriza por su baja cantidad de materia orgánica y poca retención de agua. La clase I es apta para la agricultura y se encuentra en las terrazas bajas y en las vegas de los grandes ríos. Son suelos con alta fertilidad y muy buenas condiciones de riego aptos para gran variedad de cultivos. La clase II se sitúa en la mayor parte del piedemonte; son suelos con una fertilidad más baja que los anteriores. Por su parte, la clase III se encuentra ubicada en las colinas, algunas divisorias de aguas y en la Sierra de la Macarena bajo bosques; son menos fértiles que los anteriores pero permiten riego por gravedad. La clase IV se localiza en el piedemonte con poco sembradío; son suelos de baja fertilidad, pero responden a dosis de fertilizantes permitiendo el cultivo de pastos.

La clase V se localiza en la llanura abierta; son suelos de baja fertilidad y con muy baja respuesta al abono. La clase VI está localizada en la altillanura y particularmente en zonas de pendiente donde los contenidos de hierro son bastante altos lo que impide tratamientos de mejoramiento; solo conservan el pasto natural. La clase VII se localiza en el centro y norte del departamento donde el régimen de lluvias es alto así como la evapotranspiración; los suelos son sensibles a la erosión (Figura 2.9).

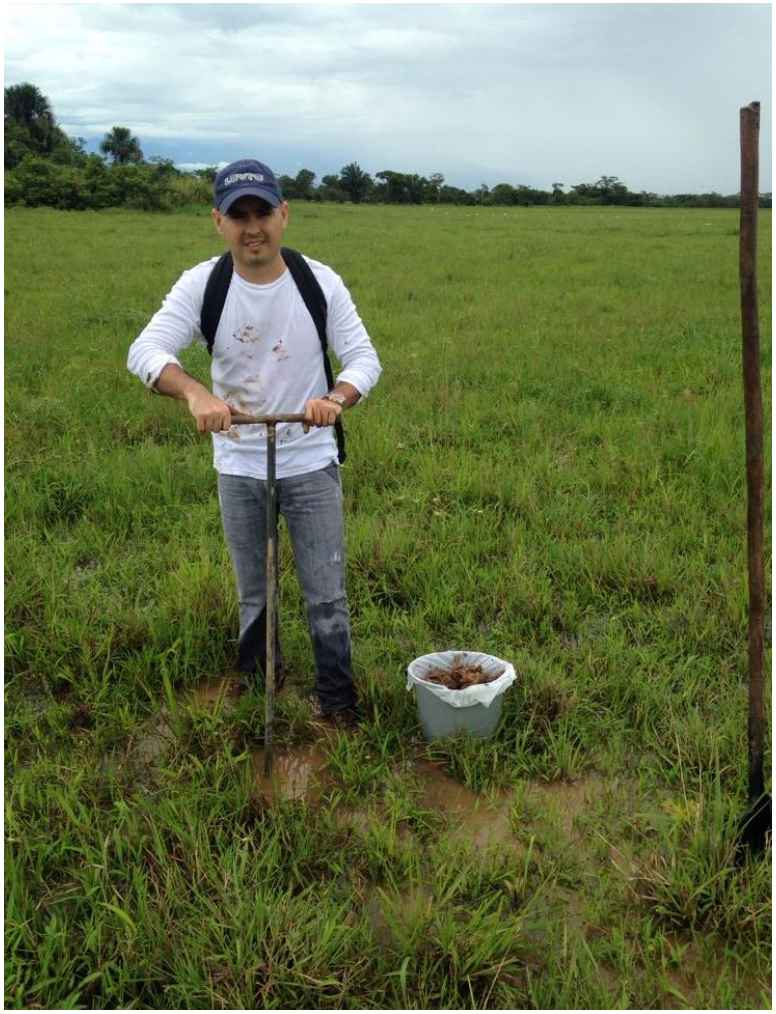

Figura 2.9 Suelos agrícolas periurbanos, irrigados con aguas potencialmente contaminadas

2.1. Infraestructura urbana del municipio de Villavicencio.

En cuanto a la infraestructura física del municipio destinada para el transporte terrestre intermunicipal e interdepartamental, existe una terminal para dicha actividad. Para el caso del transporte aéreo, la ciudad cuenta con el Aeropuerto de Vanguardia, que por el intenso flujo de vuelos comerciales hacia la Orinoquia, la Amazonia y el resto de Colombia se le considera dentro de los más importantes del país. Los principales corredores viales dentro de la ciudad se resumen a las siguientes avenidas: del Llano, Circunvalar, Alfonso López, Los Maracos y la Cuarenta, de igual manera el Anillo Vial y la vía Catama. Estos corredores se pueden relacionar de acuerdo a su función de distribuidores del transporte urbano así: Anillo vial central, Avenida del Llano, Avenida Circunvalar y Anillo Perimetral (Alcaldía de Villavicencio, 2013) (Figura 2.10).

Figura 2.10 Infraestructura vial de Villavicencio. A) Vía principal de acceso intermunicipal, alta densidad de tráfico. B) Vía principal urbana, alta densidad de tráfico. C) Vías de zonas comerciales, alta densidad de tráfico. D) Vías de zonas residenciales, baja densidad de tráfico

2.2. Diseño del muestreo de polvo de carretera y suelos periurbanos

2.2.1 Muestreo de polvo de carretera

Las muestras de polvo de la carretera se obtuvieron de puntos de los entornos urbanos de la ciudad, distribuidos en áreas clasificadas por los autores como residenciales, comerciales, centro de la ciudad, vías principales. La clasificación se realizó según la actividad predominante (Figura 2.10). Las muestras se recogieron de un marco de 0,25 m^2, utilizando cepillos de 7,6 cm y una pala de mano de plástico. Las muestras se secaron a temperatura ambiente y se homogeneizaron después de pasar a través de un tamiz de 2 mm previo al análisis y cada muestra se compone de cinco submuestras, según lo recomendado por Charlesworth et al., 2003 y Trujillo-González et al., 2016. En la tabla 2.11. se presentan las coordenadas geográficas.

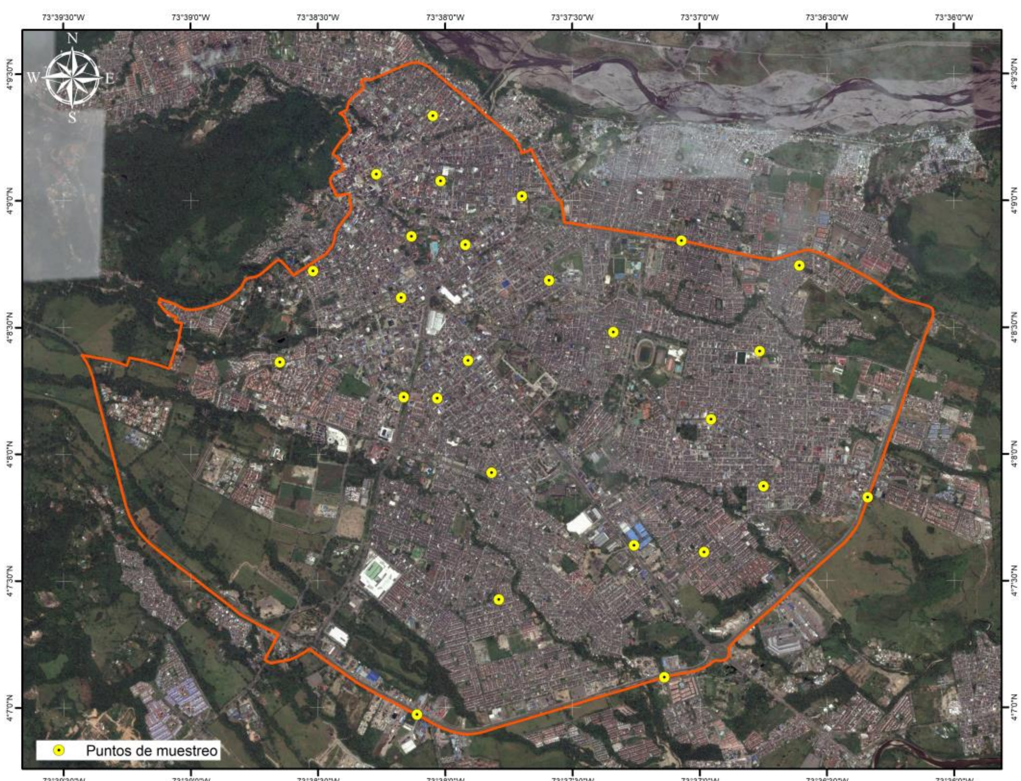

Figura 2.11 Localización espacial de los puntos de muestreo en el área urbana de Villavicencio

Tabla 2.2 Coordenadas geográficas de los puntos de muestreo del polvo de carretera.

Uso de suelo	Código	Longitud	Latitud
CENTRO	Cn2	73° 38' 8,005" W	4° 8' 51,547" N
	Cn3	73° 38' 31,204" W	4° 8' 43,346" N
	Cn1	73° 38' 16,258" W	4° 9' 6,267" N
COMERCIAL	Ct2	73° 36' 44,996" W	4° 7' 52,324" N
	Ct4	73° 37' 55,312" W	4° 8' 49,520" N
	Ct6	73° 37' 54,674" W	4° 8' 22,124" N
	Ct5	73° 38' 1,961" W	4° 8' 13,182" N
	Ct7	73° 38' 10,435" W	4° 8' 36,992" N
	Ct8	73° 38' 1,120" W	4° 9' 4,627" N
	Ct1	73° 36' 57,381" W	4° 8' 8,184" N
	Ct3	73° 36' 45,920" W	4° 8' 24,296" N
RESIDENCIAL	R6	73° 37' 35,562" W	4° 8' 41,093" N
	R1	73° 37' 47,464" W	4° 7' 25,568" N
	R2	73° 37' 49,152" W	4° 7' 55,564" N
	R5	73° 36' 36,529" W	4° 8' 44,567" N
	R8	73° 38' 2,929" W	4° 9' 20,088" N
	R7	73° 38' 39,026" W	4° 8' 21,743" N
	R4	73° 37' 20,419" W	4° 8' 28,809" N
	R3	73° 36' 59,025" W	4° 7' 36,743" N
VÍAS PRINCIPAL	Vp2	73° 38' 9,809" W	4° 8' 13,466" N
	Vp3	73° 38' 6,738" W	4° 6' 58,324" N
	Vp4	73° 37' 8,396" W	4° 7' 7,122" N
	Vp5	73° 36' 15,588" W	4° 6' 41,357" N
	Vp7	73° 36' 20,423" W	4° 7' 49,717" N
	Vp8	73° 37' 4,318" W	4° 8' 50,464" N
	Vp6	73° 37' 41,930" W	4° 9' 1,030" N
	Vp1	73° 37' 15,571" W	4° 7' 38,364" N

2.2.2 Muestreo de suelos periurbanos

Se tomaron un total de muestras de suelo a una profundidad de 0 a 30 cm considerada como la zona de importancia agrícola y donde se acumulan los metales pesados de fuentes antrópicas (Micó et al., 2006). El muestreo fue sistemático en cruz, es decir cada uno de los puntos de muestreo están a distancias uniformes, cubriendo la totalidad del área. Las muestras se recolectaron en septiembre de

2015. Cada muestra estuvo compuesta por cinco sub-muestras y los puntos de muestreo fueron ubicados con el software ArcGis 10.1, y luego en terreno se localizaron con ayuda de un GPS Garmin 62 SC (Figura 2.12). En la tabla 2.2 se presentas las coordenadas geográficas.

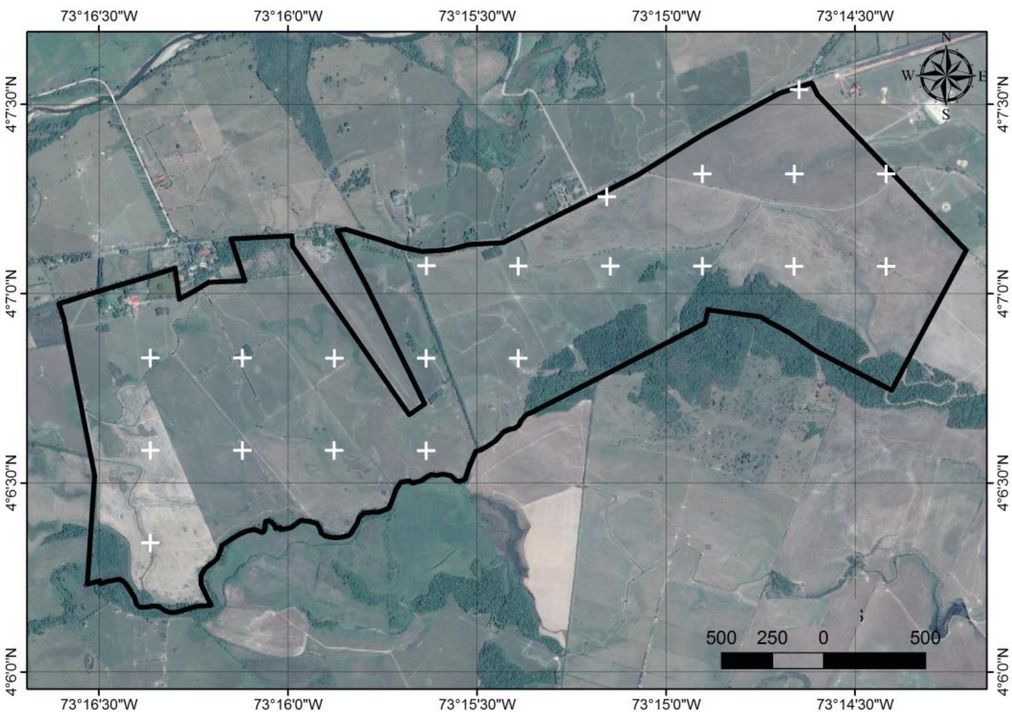

Figura 2.12 Localización espacial de los puntos de muestreo en suelos agrícolas periurbanos de Villavicencio

Tabla 2.3 Coordenadas geográficas de los puntos de muestreo de suelos agrícolas irrigados con aguas potencialmente contaminadas

Nombre del punto	Código	Coordenada Geográficas	
		Latitud	Longitud
Suelo	p1	4° 4'3.69" N	73°29'51.67" W
Suelo	p2	4° 4'4.25" N	73°29'51.64" W
Suelo	p3	4° 4'4.80" N	73°29'51.66" W
Suelo	p4	4° 4'4.97" N	73°29'51.06" W
Suelo	p5	4° 4'4.23" N	73°29'51.01" W
Suelo	p6	4° 4'3.72" N	73°29'50.98" W
Suelo	p7	4° 4'5.12" N	73°29'50.49" W
Suelo	p8	4° 4'4.37" N	73°29'50.46" W
Suelo	p9	4° 4'3.92" N	73°29'50.41" W
Suelo	p10	4° 4'5.26" N	73°29'50.02" W
Suelo	p11	4° 4'4.50" N	73°29'50.00" W
Suelo	p12	4° 4'3.90" N	73°29'50.00" W
Suelo	p13	4° 4'5.28" N	73°29'49.51" W
Suelo	p14	4° 4'4.60" N	73°29'49.56" W
Suelo	p15	4° 4'3.92" N	73°29'49.62" W
Suelo	p16	4° 4'5.35" N	73°29'49.02" W
Suelo	p17	4° 4'4.66" N	73°29'49.10" W
Suelo	p18	4° 4'4.02" N	73°29'49.19" W
Suelo	p19	4° 4'5.50" N	73°29'48.55" W
Suelo	p20	4° 4'4.72" N	73°29'48.68" W
Suelo	p21	4° 4'4.06" N	73°29'48.79" W

3. HEAVY METAL ACCUMULATION RELATED TO POPULATION DENSITY IN ROAD DUST SAMPLES TAKEN FROM URBAN SITES UNDER DIFFERENT LAND USES

Science of the Total Environment 553 (2016) 636–642

Contents lists available at ScienceDirect

Science of the Total Environment

journal homepage: www.elsevier.com/locate/scitotenv

Heavy metal accumulation related to population density in road dust samples taken from urban sites under different land uses

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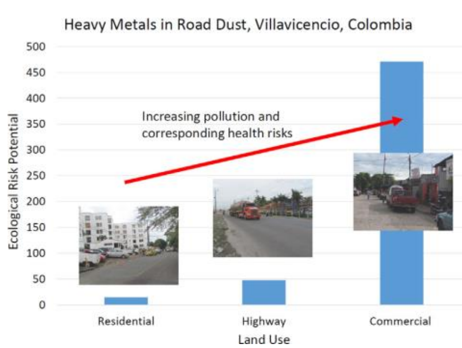
HIGHLIGHTS

- Road dust increased along with city growth and its dynamics.
- The commercial sector showed the highest concentrations of heavy metals.
- The presence of Zn, Pb and Cu in the three sectors is noteworthy.
- Road dust might cause a number of negative environmental impacts.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 12 January 2016
Received in revised form 15 February 2016
Accepted 15 February 2016
Available online xxxx

Editor: Jay Gan

Keywords:
Ecological risk index
Heavy metals
Urban dust
Urban pollution

ABSTRACT

Soil pollution is a key component of the land degradation process, but little is known about the impact of soil pollution on human health in the urban environment. The heavy metals Pb, Zn, Cu, Cr, Cd and Ni were analyzed by acid digestion (method EPA 3050B) and a total of 15 dust samples were collected from streets of three sectors of the city with different land uses; commercial, residential and a highway. The purpose was to measure the concentrations of heavy metals in road sediment samples taken from urban sites under different land uses, and to assess pollution through pollution indices, namely the ecological risk index and geoaccumulation index. Heavy metals concentrations (mg/kg) followed the following sequences for each sector: commercial sector Pb (1289.4) > Cu (490.2) > Zn (387.6) > Cr (60.2) > Ni (54.3); highway Zn (133.3) > Cu (126.3) > Pb (87.5) > Cr (9.4) > Ni (5.3); residential sector Zn (108.3) > Pb (26.0) > Cu (23.7) > Cr (7.3) > Ni (7.2). The geoaccumulation index indicated that the commercial sector was *moderately to strongly polluted* while the other sectors fell into the *unpolluted* category. Similarly, using the ecological risk index the commercial sector fell into the *considerable* category while the other sectors classified as *low* risk. Road dust increased along with city growth and its dynamics, additionally, road dust might cause a number of negative environmental impacts, therefore the monitoring this dust is crucial.

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http://dx.doi.org/10.1016/j.scitotenv.2016.02.101
0048-9697/

3. HEAVY METAL ACCUMULATION RELATED TO POPULATION DENSITY IN ROAD DUST SAMPLES TAKEN FROM URBAN SITES UNDER DIFFERENT LAND USES

Abstract

Soil pollution is a key component of the land degradation process, but little is known about the impact of soil pollution on human health in the urban environment. The heavy metals Pb, Zn, Cu, Cr, Cd and Ni were analyzed by acid digestion (method EPA 3050B) and a total of 15 dust samples were collected from streets of three sectors of the city with different land uses; commercial, residential and a highway. The purpose was to measure the concentrations of heavy metals in road sediment samples taken from urban sites under different land uses, and to assess pollution through pollution indices, namely the ecological risk index and geoaccumulation index. Heavy metals concentrations (mg/kg) followed the following sequences for each sector: commercial sector Pb (1289.4) > Cu (490.2) > Zn (387.6) > Cr (60.2) >Ni (54.3); highway Zn (133.3) > Cu (126.3) > Pb (87.5) > Cr (9.4) > Ni (5.3); residential sector Zn (108.3) > Pb (26.0) > Cu (23.7) > Cr (7.3) > Ni (7.2). The geoaccumulation index indicated that the commercial sector was moderately to strongly polluted while the other sectors fell into the unpolluted category. Similarly, using the ecological risk index the commercial sector fell into the considerable category while the other sectors classified as low risk. Road dust increased along with city growth and its dynamics, additionally, road dust might cause a number of negative environmental impacts, therefore the monitoring this dust is crucial.

3.1. Introduction

Land degradation is a worldwide process affecting the Earth system due to human use and abuse of natural resources (Brevik et al., 2015). Degradation of soils has been accelerated due to the growth of urban populations and has resulted in soil sealing, changes in albedo, in the hydrological cycle and reduced or eliminated the ecosystem services and natural resources that humankind receives from soils (Feller et al., 2015; Zornoza et al., 2015).

Road dusts accumulated in urban zones contain a diversity of materials that ranges from mineral compounds to organic and inorganic materials of anthropogenic origin that may deposit on the impermeable surfaces of cities such as roads and roofs (Shi et al., 2010). This is one part of creating the environmental problems that are triggered by the development of cities and roads, others include the increase of water and soil losses due to sealing of soils (Cerdà, 2007; Cheng et al., 2015; Seutloali and Beckedahl, 2015), and the development of increased connectivity of sediments and water (Baartman et al., 2013; Bochet, 2015; Marchamalo et al., 2015).

The heavy metal content of surface soil and street dust are good indicators of environmental accumulation of heavy metals as they act as sinks of the pollutants (Sezgin et al., 2004). Davis and Birch (2010) estimate that in urbanized basins roads may constitute 22% of the area and contribute 26% of the runoff. In our opinion even this is a conservative number, because on roads the rainfall runoff coefficient would be close to 100%. While an unsealed soil would have a rainfall runoff coefficient of about 1 to 30% (Okoński, 2007) when under natural forest; it can be to up to 80% when soils are heavily compacted or badland areas have developed (Cerdà, 1999). Road and road embankments can generate high to very high runoff volumes (Pereira et al., 2015).

Sartor and Boyd (1974) determined that the pollutant load in storm runoff from urban areas is significantly higher than in rural runoff. This, in combination with the observation that roads provide a large amount of storm runoff in urban areas, indicates that most of the pollution in urban water sources and adjacent soils may be related to road input (Vaze and Chiew, 2002). Rissler et al (2012) found that the main pollutants associated with urbanized basins are copper (Cu), lead (Pb) and zinc (Zn); together with these nickel (Ni), cadmium (Cd) and chromium (Cr) can also be found, which come from industrial activities (García and Poleto, 2014). Most heavy metals are poorly soluble, and therefore are transported through the catchment bonded to sediment particles (Loganathan et al., 2013; Morgan, 2013). Therefore, our level of understanding of the fate of the sediment associated pollutants in a catchment is highly dependent on the how well we understand the transport processes of sediment in these catchments (Rossi et al., 2013). Practices like use of vegetation buffers, storage dams, and establishment of riparian vegetation along small streams within catchments are elements that impact the cascade of sediment and can partition the amount sediment with its associated pollutants (Keesstra et al., 2012; Keesstra et al., 2014; Mekonnen et al., 2015a). Sediment transport in urban catchments is highly complex and difficult to measure and predict with modelling because of non-linear processes and bypassing of the natural system with drainage and sewer pipes (Fletcher et al., 2013; Franz et al., 2014).

Urban sediment accumulated on roads is a sink of pollutants from cities, such as heavy metals, where contact and ingestion of particles derived from these might represent serious issues for human health (Brevik, 2009; Zheng et al., 2010; Acosta et al., 2014). Pollutants affect human health in many ways; one of them is the production of quality food in the area surrounding cities as well as within cities (Roy and McDonald, 2015; Beniston et al., 2015; Brevik et al., 2016).

Based on the above, surveillance of roads that show high traffic flow and that are also in industrial areas should be a primary task for public health and risk management programs (Nazzal et al., 2012; Neff et al., 2013), as remediation of health hazards and preventing exposure to health risks are major goals of public health officials (Neff et al., 2013). Common sources of metal contaminants like Pb, Cu, Cd and Zn include the use of gasoline type fuels, tire and brake pad wear, oils, lubricants, and grease (Christoforidis and Stamatis,2009); while Cr and Ni come from the wear of metallic parts and chrome accessories (Al-Shayep and Seaward, 2001). Road sweeping and cleaning systems have been implemented in several cities around the world to mitigate the effects of rainwater runoff on urban water systems (Brinkmann and Tobin, 2001). Road cleaning is a suitable mechanism for the management of urban pollutants. According to Calvillo et al. (2015), little research has been done on the comparison of quantitative data about the efficacy of various road sediment cleaning and sweeping methods.

There is a lack of data for this region, and in general metals data and funding to conduct such work in developing countries is not abundant. Keeping in mind that new data for regions that are data deficient provides new knowledge and carries with it a certain level of uniqueness, the main goals of this study were to 1) assess the levels of select heavy metals: Cu, Pb, Ni, Zn and Cr, in dust taken from urban sites with different land uses 2) investigate the differences between geochemical background values and metal levels, and 3) calculate pollution indices to assess the level of pollution as a tool for urban sanitation decision-making.

3.2. Materials and methods

3.2.1. Study area

The study took place in the urban area of the city of Villavicencio, located in mid-eastern Colombia (Figure 3.1). Its coordinates are 4°15'48''N – 73°65'49''W, its annual average temperature is 25.6°C, annual average rainfall is 3700mm, and mean elevation is 467 m.a.s.l. Villavicencio is one of the cities with the highest urban growth rate over the last decade in the country, with an estimated population in 2014 of 473,718 inhabitants (DANE 2010). The of population growth rate in the city of Villavicencio is 2.3 % per annum. Geomorphologically, soils of the region are located on upper and middle terraces, which initially were tropical grasslands with native grasses. The lower terraces, including the catchment area of the river Ocoa, were covered by gallery forest. The natural vegetation is tropical rain forest but that has been mostly removed to establish agricultural fields with production characteristics different from agriculture in the foothills. Many soils were incorporated into agricultural production and then occupied by urban or periurban uses. Soils in the study area are dominated by Inceptisols and Oxisols as classified by the USA Soil Taxonomy system (Goosen, 1971), which often translate to Cambisols or Ferralsols in the FAO-ISRIC-ISSS system.

3.2.2. Sampling system

A total of 15 sediment samples were collected from the streets of three sectors of the city with different land uses (commercial, residential and highway); sampling was carried out between March and April 2014. Background metal levels were taken from Fadigas et al. (2006), as the data in this paper is considered to be representative for the background levels in this area. Fadigas et al. (2006) conducted their heavy metal analyzes using extraction with aqua regia and inductively coupled plasma analysis (ICP-AES). Samples were collected from a frame of 0.25 m2, using 7.6 cm brushes and a plastic hand-shovel; different equipment was used to collect the samples at each site. The samples were dried at room temperature and homogenized with a 2 mm sieve previous to analysis, as described by Charlesworth et al. (2003). Each sample was composed of five subsamples.

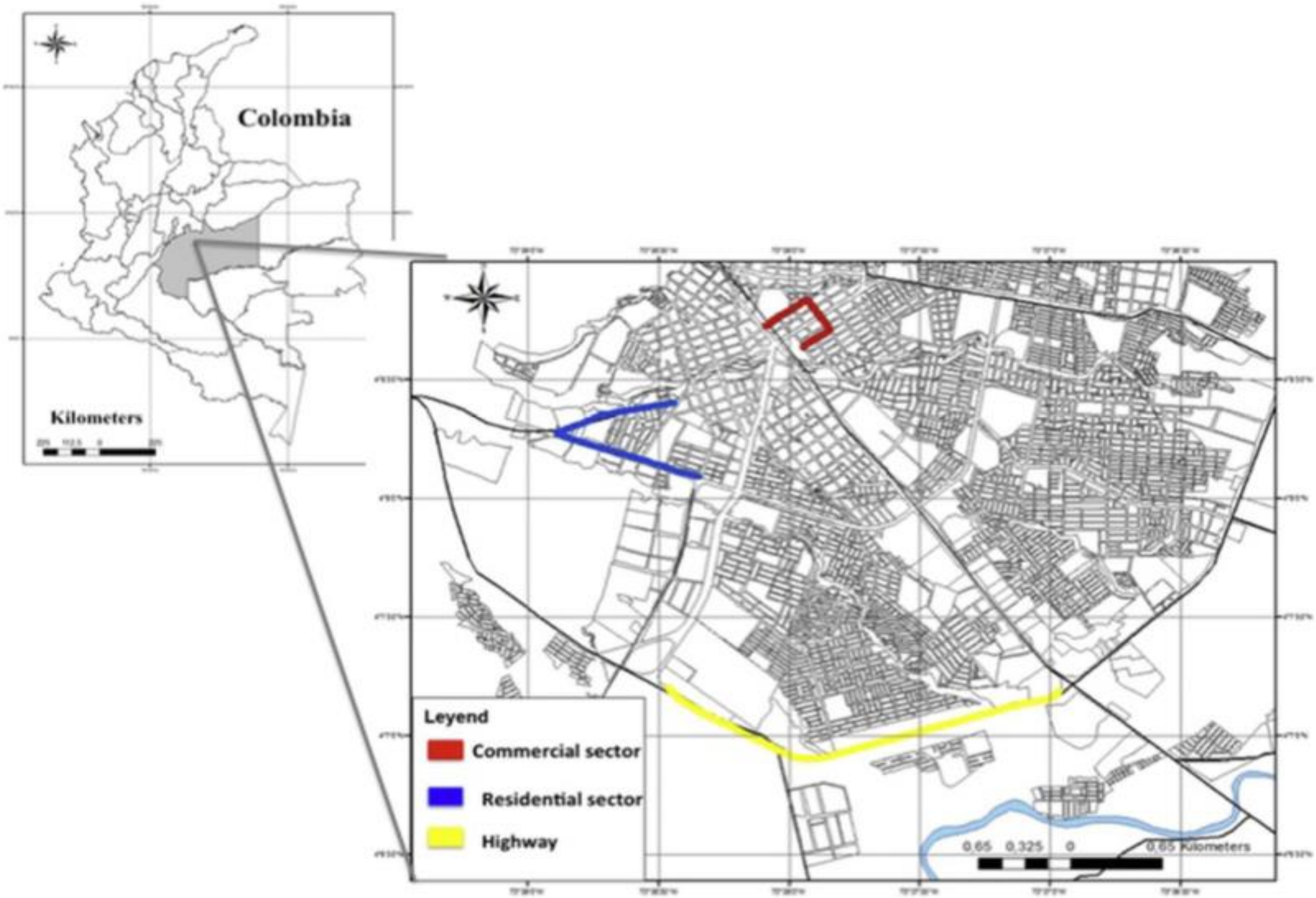

Figure 3.1 Geographic location and boundaries of the study area, Villavicencio, Colombia. The area delimited with yellow represents the highway, blue represents the residential sector and red corresponds to the commercial sector of the city used in this study

3.2.3. Chemical analyses

Determination of the concentrations of total heavy metals (Cu, Pb, Ni, Zn, Cr) was carried out according to the nitric acid, hydrochloric acid and hydrogen peroxide digestion method, and then analyzed by atomic absorption spectrophotometry using air-acetylene flame, 3050 B (USEPA, 1996). Quality control was assured by the use of duplicates. Also quality control included the use of a method reagent blank and several certified reference materials to check accuracy and precision of the analytical data.

3.2.4. Statistical methods

Standard deviation (SD) was calculated and the method's detection limit (MDL) was calculated using the following formula: MDL = mean + (2 × SD). Calculated MDL were 1.5 mg/kg (Pb), 0.12 mg/kg (Ni), 0.010 mg/kg (Zn), 0.038 mg/kg (Cu), 0.014 mg/kg (Cd) and 0.076 mg/kg (Cr).

3.2.5. Pollution indices

Ecological risk (RI) (Hakanson, 1980) and geo-accumulation (I-geo) (Müller, 1969) indices were applied, which are established methodologies to assess the impact of heavy metals on the environment (Atiemo et al., 2011; Saeedi et al., 2012; García-Martínez and Poleto, 2014). I- geo (Müller, 1969) was calculated as follows:

$$Igeo = Log_2 \frac{Cs}{1.5 \times Bn} \qquad [1]$$

Where Cs refers to calculated values and Bn to background values, the factor 1.5 is applied in order to control the variations of Bn values caused by the environment. Shi et al. (2010) and García-Martínez and Poleto (2014) identified seven categories of I-geo, shown in Table 3.1. Ecological risk index (RI) (Hakanson, 1980) integrates the factors of ecological risk potentials of each metal and associates their ecological and environmental effects with their toxicology (Ogunkunle and Fatoba, 2013). The calculation method is given in Eq. (2):

$$RI = \sum Er^i ; Er^i = Tr^i * C_f^i ; \; C_f^i = \frac{C_{o-1}^i}{C_n^i} \qquad [2]$$

Where, C_f^i corresponds to the pollution factor for each metal, C_{o-1}^i is the concentration of a heavy metal in the sample, Cin corresponds to the background value, Er^i is the ecological risk potential of each metal, Tr^i is the toxic response coefficient developed by Hakanson (1980), toxic response coefficients are Cd (30), Cu (5), Cr (2), Zn (1), Pb (5) and Ni (3), and finally RI is the ecological risk index. The interpretation categories for RI are shown in Table 3.2. For the indices, the background values determined by Fadigas et al. (2006) were applied, and those background values are 0.5 mg/kg (Cd), 35.1 mg/kg (Cu), 40.2 mg/kg (Cr), 59.9 mg/kg (Zn), 17 mg/kg (Pb) and 13.2 mg/kg (Ni).

Table 3.1 Geo-accumulation index assessment (Müller 1969)

Value	Category
I-geo ≤ 0	Unpolluted
0 < I-geo < 1	Unpolluted to moderately polluted
1 < I-geo < 2	Moderately polluted
2 < I-geo < 3	Moderately to highly polluted
3 < I-geo < 4	Highly polluted
4 < I-geo < 5	Highly to extremely polluted
I-geo ≥ 5	Extremely polluted

Table 3.2 Interpretation categories of the pollution factor, potential ecological risk and ecological risk index (Hakanson 1980)

Potential ecological risk		Risk index	
Value	Category	Value	Category
$Er^i < 40$	Low	$RI \leq 150$	Low
$40 \leq Er^i < 80$	Moderate	$150 \leq RI < 300$	Moderate

$80 \leq Er^i < 160$	Considerable	$300 \leq RI < 600$	Considerable
$160 \leq Er^i < 320$	High	$600 \leq RI$	Very high
E $Er^i \geq 320$	Very high		

3.3. Results and discussion

3.3.1. Metal concentrations

Heavy metal concentrations and summary statistics for the studied sectors are shown in Table 3.3. It has been pointed out that road dust resuspension contributes significantly to heavy metal concentration levels in urban areas (Karanasiou et al., 2009; Athanasopoulou et al., 2010). The commercial sector showed the highest concentrations of all the heavy metals sampled during this research. Based on the concentration of metals in each sector, they can be classified as follows; commercial sector > highway sector > residential sector. Metal concentrations in each sector followed the sequence: commercial sector Pb > Cu > Zn > Cr > Ni, highway sector Zn > Cu > Pb > Cr > Ni, residential sector Zn > Pb > Cu > Cr > Ni. Cadmium concentration did not exceed the detection limit in any of the three sectors that were assessed. Likewise, these metals widely varied between sampled sectors and between samples, due to sample heterogeneity and to several variables that cannot be controlled in between each sampling; this can be explained by the high degree of variability of the metals (Table 2.3) regardless of the distinctive economic activities in each sector. The presence of Zn, Pb and Cu in the three sectors is noteworthy. All these metals are related to traffic, state of the roads, tire and brakes wear, lubricants, and paints and fuels (García-Martínez and Poleto, 2014; Kamani et al. 2015). Probably the two main sources of street dust, and consequently of the trace elements found therein, are deposition of previously suspended particles (atmosphere aerosol) and displaced urban soil (Ferreira-Baptista and De Miguel, 2005; Han et al., 2007). In the city of Villavicencio the commercial sector generates this kind of waste, without any management protocols, due to the activities of automobile mechanics that take place there. It can be concluded that road traffic resuspended dust in Villavicencio was the largest source of the dust emissions.

One extreme measurement was found in the Pb concentration on commercial roads with a mean value of 1289.4 mg/kg that exceeded by far the 17 mg/kg reference value (Fadigas et al., 2006), just as it exceeded the maximum permissible values for commercial sectors as legislated by Mexico (400 mg/kg) (NOM-147-SEMARNAT/SSA1, 2004) and Argentina (500 mg/kg) (Decreto 831, 1993). The mean concentrations recorded for Pb suggested that automobile emissions and secondary industrial combustion processes were responsible for Pb deposition. In the highway sector Pb concentration was 87.5 mg/kg and in the residential sector 26 mg/kg. So even though they exceeded the reference values, they remain well below the permissible values in residential and commercial sectors as allowed by Mexico and Argentina. Both average and high values for the other metals were below typical limits established by several countries (Morgan, 2013). Copper is a heavy metal used in numerous applications because of its physical properties. It usually accumulates in the soil surface as a consequence of anthropogenic activities. Zinc may be derived from mechanical abrasion of vehicle parts, as it is used in the production of brass alloy, brake linings, oil leak sumps and cylinder head gaskets. Soil pollution due to accumulation of pollutants over a period of years is usually not as severe as pollution resulting from accidental or deliberate spill of industrial wastes, but atmospheric deposition can affect large areas depending on the distribution of population and industrial activities. Hence it is important for regulatory agencies to focus their efforts on sources that alter soil com- position (Guvenç et al., 2003).

Pearson correlation analysis (Table 3.4.) indicates that most of the metals are highly correlated. The Pb-Zn, Pb-Cr, Ni-Zn, Ni-Cu, Ni-Cr, Zn-Cu, Zn-Cr and Cu-Cr couples showed significant correlations with P b 0.01, and Pb-Cu were significantly correlated with $P < 0.05$. Pb-Ni showed a moderately positive but not significant correlation ($r = 0.449$). All of this points to a possible common source or sources shared by these metallic elements. The highest correlation coefficients were for Ni, Cu, Cr and Zn ($r > 0.900$); Cr and Ni are associated with paints used in automobile coatings, whereas Zn and Cu are related to the wear of automotive parts (De Miguel et al., 1997; Zafra-Mejía et al., 2013). Atiemo et al. (2011) and Saeedi et al. (2012) also found high correlation between metals, thus indicating possible shared anthropogenic source(s). In general, traffic and activities that take place in these sectors are potential sources of heavy metals. Pb, has been associated with fuel use; however, the gradual change to unleaded fuels leaves the question whether there is a current source of metal or if these are accumulations from some time ago. According to De Miguel et al. (1997), factors such as high temperature and exposure to weather accelerate corrosion processes, causing wear of metal parts which often consist of alloys of Zn, Cu, and Ni, among others, eventually resulting in the release of metals to the urban environment and their accumulation in road dust.

3.3.2. Pollution indices

The utilization of pollution indices allowed the studied sectors to be categorized based on the concentration of each metal, and when these were analyzed using I-geo it was found that the commercial sector was associated with the category *moderately to strongly polluted* with the elements Pb, Cu and Zn; while in the remaining sectors the category unpolluted was dominant. This can be associated with the socio-economic activities that take place in the commercial sector, where many low-tech auto repair services are located, while there is a severe lacks of protocols for proper waste management and disposal of materials like oils, greases, paints, fuels, metal filings and used tires.

Table 3.3 Metal concentrations, geo-accumulation index, and ecological risk index compared to background values from Fadigas et al. (2006)

Z		**Concentrations in mg/Kg**					**Geo-acumulation index I-geo**					**Ecological risk index RI**
Parameter		**Pb**	**Ni**	**Zn**	**Cu**	**Cr**	**Pb**	**Ni**	**Zn**	**Cu**	**Cr**	Integrate (Pb,Ni,Zn,Cu,Cr)
Highway	**Average**	87.5	5.3	133.3	126.3	9.4	0.8	-2.1	0.5	0.9	-2.7	47.6 (*Low*)
	Min	26.4	3.0	85.6	24.9	6.1	0.0	-2.7	-0.1	-1.1	-3.3	
	Max	326.2	10.4	189.8	248.1	14.0	3.7	-0.9	1.1	2.2	-2.1	
	SD	133.5	3.2	53.5	91.5	3.0	1.6	0.8	0.6	1.3	0.4	
Residential sector	**Average**	26.0	7.2	108.3	23.7	7.3	0.0	-1.5	0.3	-1.3	-3.1	14.8 (*Low*)
	Min	17.5	6.5	104.4	13.6	4.7	-0.5	-1.7	0.2	-2.0	-3.7	
	Max	31.7	8.9	113.8	40.0	10.0	0.3	-1.2	0.3	-0.4	-2.6	
	SD	4.7	0.9	4.1	9.6	1.9	0.3	0.2	0.1	0.6	0.4	
Commercial sector	**Average**	1289.4	54.3	387.6	490.2	60.2	4.9	1.2	2.0	2.6	-0.3	470.9 *(Considerable)*
	Min	259.2	20.7	222.5	36.1	27.1	3.3	0.1	1.3	-0.5	-1.5	
	Max	4079.8	123.3	511.8	903.0	115.3	7.3	2.6	2.5	4.1	0.9	
	SD	1598.8	41.3	129.0	345.9	35.7	1.6	1.0	0.6	1.9	1.0	
Background		17.0	13.2	59.9	35.1	40.2						

I-geo for Pb in the commercial sector was 4.9, which exceeds the values found by García-Martínez and Poleto (2014) in the city of Porto Alegre, where the I-geo was 1.75, while the population of this city is over a million, which is much larger than Villavicencio. It also exceeded the value of 2.32 reported for Shanghai, China (Shi et al., 2010) and the mean value of 1.81 (range 0.61–2.35) reported for seven cities in China (Wei and Yang, 2010). In the case of Cu, the maximum I-geo was 4.1 in the residential sector, which also exceeds the value of 1.48 found in Shanghai (Shi et al., 2010) and the 1.48 mean (range 0.86–1.93) found for seven cities in China (Wei and Yang, 2010). Finally, I-geo for Zn was 1.3 which is lower than the value of 3.04 reported in Porto Alegre (García-Martínez and Poleto, 2014), the 2.44 value reported for Shanghai (Shi et al., 2010), and the 1.48 mean (range 1.05–2.57) reported for seven Chinese cities (Wei and Yang, 2010).

Ecological risk potential for the highway and residential sectors was determined as low with RI values of 47.6 and 14.8 respectively. On the other hand, the commercial sector largely exceeded that, reaching an RI value of 470.9, placing this sector in the considerable risk category. In studies conducted in cities like Tehran, the ecological risk index was very high in all the assessed sectors (Saeedi et al., 2012), however the population of this city is more than seven million people and industrial activities are diverse. The results obtained in this study are in agreement with Saeedi et al. (2013), who reported that Pb and Zn concentrations in street dust were higher than those in urban soils.

In response to this problem, several cities around the world currently have coordinated sweeping and street cleaning systems that collect dusts in containers intended for pollutants such as heavy metals, among others (Calvillo et al., 2015). In this sense, the Pan American Health Organization (PAHO) stated that “street cleaning services is an issue of increasing concern for local governments and proper disposal of solid waste is an imperative for cities that wish a healthy habitat” (Fernández, 2002). The problem does not end with street sweeping, but other concerns arise such as; ‘How to treat rainwater that incorporates the pollutants that are not collected?' and 'How to handle the tons of sediment that are collected daily?' For the latter, material recycling and reuse potential should be considered as an option, right after proper decontamination treatment, because of the high costs of taking contaminated materials to landfills (Brinkmann and Tobin, 2001; Tobin and Brinkmann, 2004; Taylor and Owens, 2009).

These questions require investigation into how sediment and water routes through the city. How does rainwater drain from roads? Does it go into the natural river system or does it go into the sewer system? And if it goes into the sewer system, what does that drain into? Is the sewage treated in water treatment plants, and are the treatment plants equipped to clean heavy metals from the water? The water management of the city needs to be looked at in a holistic way. For this a solid understanding of the water and sediment dynamics within the catchment is needed. Hydrological dynamics are relatively well understood, although man-made structures in the urban environment highly complicate the routes water can take (Bolund and Hunhammar, 1999; Lerner, 2002).

Table 3.4 Pearson´s correlation coefficient between heavy metals in road dust samples (n = 15)

		Lead	Nickel	Zinc	Copper	Chrome
Lead	Pearson	1.00	0.449	0.713**	0.548*	0.643**
	Sig. (bilateral)		0.093	0.003	0.034	0.010
Nickel	Pearson	0.449	1.00	0.869**	0.912**	0.966**
	Sig. (bilateral)	0.093		0.000	0.000	0.000
Zinc	Pearson	0.713**	0.869**	1.00	0.944**	0.931**
	Sig. (bilateral)	0.003	0.000		0.000	0.000
Copper	Pearson	0.548*	0.912**	0.944**	1.00	0.909**
	Sig. (bilateral)	0.034	0.000	0.000		0.000
Chrome	Pearson	0.643**	0.966**	0.931**	0.909**	1.00
	Sig. (bilateral)	0.010	0.000	0.000	0.000	

* Correlation is significant with p 0.05 (bilateral).
** Correlation is significant with p 0.01 (bilateral).

However, in the case of heavy metal transport coming from roads, as is presented in this study, sediment transport is much more important to get a grip on. Due to large variations in topography and manmade sinks in the urban landscape where sediments can accumulate and form problems of different kinds this is a complex undertaking. Concepts like connectivity (Fryirs, 2013) and sediment delivery ratio (De Vente et al., 2007) can be helpful to look into the sediment dynamics within an urban catchment. Models under development (e,g. Bonumá et al., 2014; Keesstra et al., 2014) will need to incorporate urban structures and for this the connectivity concept will be most helpful. Another important issue when studying sediment dynamics at the catchment scale is the issue of large differences in the amount of sediment transported over time. Sediment tends to move in pulses and move during rare storm events. A highly complex system such as an urban environment makes the assessment of where the sediment is going already very difficult, let alone prediction of what will happen in the future. The consequences of this sediment movement can be significant. Areas located downstream from cities often include wetlands, deltas, and agricultural lands; all areas vulnerable to pollution (McCarthy et al., 2012; Conaway et al., 2013). Therefore, understanding the whole urban system in terms of water and sediment dynamics will be of utmost importance for managers in the municipalities. With this understanding proper measures can be designed and implemented to ensure polluted sediment does not get to vulnerable sites downstream. Potential measures can be sought on three levels: on site by reducing the pollutants at their origin. Second in their transfer path in the urban environment by constructing proper sewage transport and sewage water treatment, and third by implementing measures to trap sediments in the areas outside of the city boundaries using structural and vegetative measures in the river courses (cf. Mekonnen et al., 2015b). All of these measures will have positive impacts on human health (Brevik, 2009; Helmke and Losco, 2013).

3.4. Conclusions

Road dusts are a problem that increases with the growth and the dynamics of cities, and may account for many environmental impacts. In the city of Villavicencio, Colombia, it was found that the highest concentrations of heavy metals were in the commercial sector where “rudimentary” auto-repair activities take place and little regulation regarding waste management is implemented. Heavy metal road dust content in these areas exceeded background values of heavy metals. According to the concentrations in each sector, commercial metal contents > highway > residential. Through the application of the geo-accumulation index, it was confirmed that the commercial sector is characterized as a moderately to strongly polluted area, with the heavy metals primarily responsible for this classification being Pb, Cu and Zn, which are linked to socioeconomic activities in the commercial area. These elements are also present on highways, but in lower concentrations. Similarly, the ecological risk index classified the commercial sector as an area with considerable risk, while the highway and residential sectors were categorized as low risk areas. Finally, it is stated that the final disposal of road dust waste produced in cities is a major challenge, because these road dusts contain pollutants such as heavy metals that may cause public health issues and damage to natural systems. These data indicate that we need a better understanding of the fate of these pollutants, such as when and where they are entering the environment. Storm water will erode the pollutants from roads and transport them to waterways. Because heavy metals typically are absorbed to sediment particles, understanding the sediment dynamics in urban catchments is of specific interest in the context of urban catchment management and public health. Concepts like connectivity and sediment delivery ratio may serve to aid in understanding and mitigating the off-site environmental and human health damages these urban pollutants may cause.

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4. LAND USE DEPENDENT SPATIAL VARIATION AND EXPOSURE RISK OF HEAVY METALS IN ROAD-DEPOSITED SEDIMENT IN VILLAVICENCIO, COLOMBIA

Environ Geochem Health
https://doi.org/10.1007/s10653-018-0160-6

CrossMark

ORIGINAL PAPER

Land-use-dependent spatial variation and exposure risk of heavy metals in road-deposited sediment in Villavicencio, Colombia

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Received: 7 March 2018 / Accepted: 20 July 2018

Abstract Urbanization-induced land-use changes cause several environmental problems, especially in developing countries due to a lack of sufficient urban planning. This study was performed in a medium-size city of Villavicencio, Colombia. Copper, lead, nickel, zinc, chromium, manganese, and cadmium in road-deposited sediment (RDS) from different land uses were determined. Multiple geo- and statistical approaches of geographic information system mapping, Pearson correlation, Kruskal–Wallis H, hierarchical cluster analysis (HCA), and principal component analyze (PCA) were employed to assess the influence of land use on the metals' spatial distribution. The enrichment of given metals in RDS was evaluated by geo-accumulation (I_{geo}) and pollution load (PLI) indexes. The exposure human health risk was assessed by hazard index (HI). Results show that the average contents of the given metals decreased in the order of commercial [residential [highway [government institutions and public parks areas. Commercial areas thereafter always have the highest metals enrichment (I_{geo}) and pollution level (PLI). HI assessment indicates that child has a higher health risk than adult due to the exposure to metals in RDS. HCA analysis reveals that surface roughness had a more direct influence than land-use type on metals' distribution. Kruskal–Wallis H test further suggests land-use type had a significant influence on certain metals' spatial variation. Two potential (group) sources of geochemical and vehicular sources, along with leaded petrol and paintings, were inferred to be the main contributors to metals in RDS by PCA analysis.

Keywords Heavy metal · Geo- and statistical analysis · Risk assessment · Road-deposited sediment · Spatial variation

Electronic supplementary material The online version of this article (https://doi.org/10.1007/s10653-018-0160-6) contains supplementary material, which is available to authorized users.

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Published online: 27 July 2018

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Abstract

Urbanization induced land-use changes cause several environmental problems, especially in developing countries due to a lack of sufficient urban planning. This study was performed in a medium-size city of Villavicencio, Colombia. Copper, lead, nickel, zinc, chromium, manganese, and cadmium in road-deposited sediment (RDS) from different land uses were determined. Multiple geo- and statistical approaches of geographic information system (GIS) mapping, Pearson correlation, Kruskal-Wallis H, hierarchical cluster analysis (HCA), and principal component analyse (PCA) were employed to assess the influence of land use on the metals' spatial distribution. The enrichment of given metals in RDS was evaluated by Geo-accumulation (Igeo) and Pollution Load (PLI) indexes. The exposure human health risk was assessed by Hazard Index (HI). Results show that the average contents of the given metals decreased in the order of commercial > residential > highway > government institutions and public parks areas. Commercial areas thereafter always have the highest metals enrichment (Igeo) and pollution level (PLI). HI assessment indicates that child has a higher health risk than adult due to the exposure to metals in RDS. HCA analysis reveals that surface roughness had a more direct influence than land-use type on metals' distribution. Kruskal-Wallis H test further suggests land-use type had a significant influence on certain metals' spatial variation. Two potential (group) sources of geochemical and vehicular sources, along with leaded petrol and paintings were inferred to be the main contributors to metals in RDS by PCA analysis.

4.1. Introduction

Urbanization is likely to be one of the defining phenomena of the 21st Century for Latin America and the Caribbean (LAC) as well as the rest of the world (Van Haeften, 2010). According to United Nations estimates, in LAC, the number of people living in urban areas will increase by about 127 million between 2007 and 2025 (UN, 2014). It represents a 28 % increase in the region's urban population in less than 20 years, and over 85 % of the total population lives in the urban areas (UN, 2014; Beal et al., 2017). However, the rapid urbanization and land-use changes (agriculture, mining, logging, housing, recreation, etc) would lead to a severe damage of the natural resources and ecosystems (Zhang et al. 2017a; Zhang et al. 2017b). It causes many problems such as land insecurity; water, air, and soil pollution; noise and waste disposal; loss of wildlife habitats and biodiversity (Zornoza et al., 2015).

Road-deposited sediment (RDS), also known as road dust, road particle, and roadside sediment, urban diffuse pollutant, often contains elevated contents of pollutants (Zhang et al. 2015a; Zhang et al. 2015c). Increasing studies reported the influence of RDS associated contaminants in contribution to the pollution loads of urban surface runoff and ambient airborne particulate matter (Calvillo et al, 2015). Typically, RDS consists of eroded rock and soil, leaves and organic debris; it also contains the anthropogenic materials such as eroded material from bricks, concrete, trash, building materials, construction track out, and roadway debris (maintenance/traction sand, automotive debris, exhaust particles, asphalt, sealants, etc.) (Zhang et al. 2015b; Zhang et al. 2015c). Since RDS is a temporary sink of the various pollutants, its pollution level is a potential indicator for characterizing urban environmental quality.

Among such pollutants in RDS, heavy metals are of concern because of their environmental persistence, biogeochemical recycling, and toxicity risks (Zhang et al. 2015a, 2017a). Some of them are toxic even if their contents are at a trace level and their toxicity increases with accumulation in the environment. Anthropogenic activities, such as vehicular traffic, industrial plants, power generation facilities, construction materials, and residential fossil-fuel burning could boost metals' environmental load and further pose higher potential risks to human health and ecological system, which is a challenge to land-use planning and decision-making process (Czarnecki and Düring, 2015; Charlesworth et al., 2011; Garcia and Jiménez-Ballesta, 2017; Trujillo-González et al., 2017). Concerning this issue, in recent decades, contamination levels (Trujillo-González and Torres-Mora, 2015), spatial distributions (Amato et al., 2009; Lui et al., 2014), chemical fractionation (Świetlik et al., 2015), source identification (Zhang et al. 2015b), and ecological and human health risk assessments (Soltani et al., 2015; Ebqa'ai et al., 2017) of metals in RDS have been investigated worldwide. However, comparably few studies have been conducted in medium-sized Latin American cities with less than one million inhabitants. In general, in these countries, there are few studies aimed at evaluating the influence of urbanization on the pollution distribution in RDS.

To assistant the heavy metal mitigation strategies, consequently, the primary objective of this was to provide reference data to legislators, planners, state and local government officials to better understand the influence of land use pattern on the pollution hotspots and health risk of metals in RDS. The detailed objectives were to (i) determine the spatial distribution of metals in RDS in the city of Villavicencio, (ii) assess the effect of land use on the metals' spatial distribution, (iii) assess the enrichment and exposure health risk assessment posed by metals in RDS, and (iv) identify the primary regional source contributors to metals in RDS.

4.2. Materials and methods

4.2.1. Study area

This study took place in the city of Villavicencio (4º154´8´N – 73º654´9´W), mid-eastern Colombia as given in Figure 4.1. The annual average temperature in this city is 25.6 ºC; the annual average rainfall is 3700 mm, and the mean elevation is 467 m. Villavicencio is a medium-sized city with the highest urban growth rate over the last decade in Colombia, with a population in 2017 of above 500 thousand inhabitants and an average increase rate of 2.30% per year among 2010-2017 (DANE, 2010; Torres-Mora and Trujillo-Gonzalez, 2014). The economic activities are distributed as follows: 37% is commercial activities (dedicated to tourism and informality); 23% is services (restaurants, hotel etc); 12% is transportation and activities of automobile mechanics; 8% is industry; 8% is construction; 7% is real estate; 5% is the others (livestock and agriculture) (Vargas-Pabón, 2011).

4.2.2. Sample collection

RDS samples were collected from 27 sampling sites with different land-use types of residential, commercial, government institutions and public parks (GP), and highway in November and December of 2016, which considered as the beginning of the drought season with average monthly rainfalls of 373.4 mm and 197.1 mm respectively, as given in supplementary material Table S1. Samples were collected within a frame of 0.25 m2, using 7.6 cm brushes and a plastic hand-shovel. The collected samples were air dried under the room temperature and homogenized after passing through a 2 mm sieve previous to laboratory analysis (Charlesworth et al., 2003; Trujillo-Gonzalez et al., 2016). Each sample was composed of five subsamples according to the laboratory protocol of our previous study (Trujillo-González et al. 2016).

4.2.3. Chemical analyses

According to the nitric acid (HNO_3), hydrochloric acid (HCl) and hydrogen peroxide (H_2O_2) digestion method, concentrations of copper (Cu), lead (Pb), nickel (Ni), zinc (Zn), chromium (Cr), manganese (Mn), and cadmium (Cd) were determined by flame atomic absorption spectrometry (FLAA, 3050B) (USEPA, 1996).

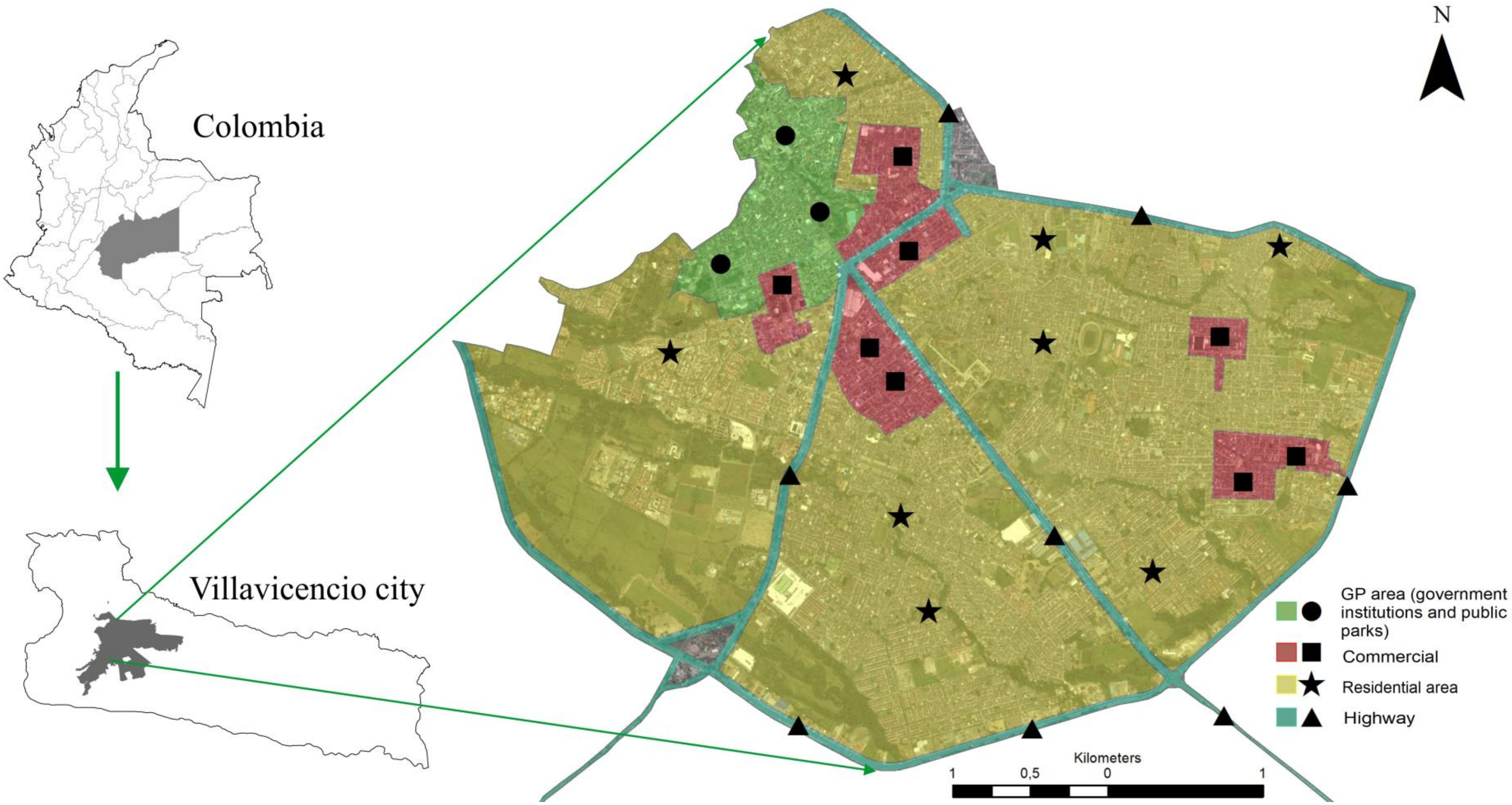

Figure 4.1 Map of sampling sites in the city of Villavicencio, Colombia

Briefly, 1 g RDS sample was deposited into a 50 ml glass beaker containing 4 ml of HNO3, 10 ml of HCl and 2 ml H2O2. Afterward, all beakers were covered and digested for 2 h. The digested samples were filtered and transferred to a 25 ml volumetric flask. Quality control was assured by using duplicates. Reagent blank and several certified reference materials were used to check the accuracy and precision of the analytical data. Analysis of certified reference materials (High-Purity Standards) indicated that the recovery of Cu, Pb, Ni, Cr, Cd, and Zn was 100± 20%. Chemicals were analytical grade (MERCK).

4.2.4. Enrichment assessment

The geo-accumulation index I_{geo}, proposed by Muller (1969), was applied to assess the enrichment of metals. The geo-accumulation index is expressed as follows:

$$Igeo = Log_2 \frac{Cs}{1.5 \times Bn} \qquad \text{Eq. 2.1}$$

Where Cs refers to the determined concentrations, and B_n refers to background values. A factor of 1.5 is applied to control the variations of B_n values. Muller (1969), García-Martínez and Poleto (2014) and Trujillo-Gonzalez et al. (2016) classified the enrichment levels into seven classes as: G0 unpolluted if $I_{geo} \leq 0$; G1 unpolluted to moderately polluted if $0 < I_{geo} < 1$; G2 moderately polluted if $1 < I_{geo} < 2$; G3 moderately to highly polluted if $2 < I_{geo} < 3$; G4 highly polluted if $3 < I_{geo} < 4$; G5 highly to extremely polluted if $4 < I_{geo} < 5$; and G6 extremely polluted if $I_{geo} \geq 5$.

Pollution Load Index (*PLI*) was used to assess the pollution level of metals in the study areas. *PLI* was calculated using the following equations (Tomlinson et al., 1980):

$$CF_i = C_i / C_{oi} \qquad \text{Eq. 2}$$

$$PLI = \sqrt[n]{CF_1 \times CF_2 \times \ldots \times CF_n} \qquad \text{Eq. 3}$$

Where CF_i is the contamination factor for metal *i*; C_i is the metal concentration in the sample; C_{oi} means the background value of metal *i*; and *PLI* reflects the integrated pollution of multiple metals in a sample. Based on the *PLI* pollution levels, we adopted the classification standards in this study as follows: non-pollution if *PLI* (*CF*) ≤ 1; slight pollution if 1 < *PLI* (*CF*) ≤ 2; moderate pollution if 2 < *PLI* (*CF*) ≤ 3; and heavy pollution if *PLI* (*CF*) > 3. The reference values for I_{geo} and *PLI* indexes calculation were those from literature (Fadifas et al., 2006, Rueda et al., 2011, Mahecha-Pulido et al., 2015), namely, Cd = 0.5 mg kg^{-1}, Pb = 17 mg kg^{-1}, Ni = 13.2 mg kg^{-1}g, Cu = 35.1 mg kg^{-1}, Zn = 59.9 mg kg^{-1}, and Cr = 40.2 mg kg^{-1}, Mn 600 mg kg^{-1}.

4.2.5. Exposure human health risk assessment

Exposure to metals in RDS can occur in three routes: (i) direct particle ingestion (Ding); (ii) suspended particle inhalation through the mouth and nose (Dinh), and (iii) dermal absorption of particles adhered to the skin (Ddermal). The dosage received through each route was estimated using the Equations 4 - 6 (USEPA, 1996, 1989). The Lifetime Average Daily Dose (LADD) for carcinogens was used for the exposure via inhalation of Cd, Cr, and Ni in the cancer risk evaluation expressed in the Equation 7 (USEPA, 1996, 2001). The symbols and parameters of Equation 4 - 7 are shown in Table 4.1.

$$D_{ing} = C \times \frac{R_{ing} \times EF \times ED}{BW \times AT} \times 10^{-6} \qquad \text{Eq. 4}$$

$$D_{inh} = C \times \frac{R_{inh} \times EF \times ED}{PEF \times BW \times AT} \qquad \text{Eq. 5}$$

$$D_{dermal} = C \times \frac{SA \times SL \times ABS \times EF \times ED}{BW \times AT} \times 10^{-6} \qquad \text{Eq. 6}$$

$$LADD_{inh} = \frac{C \times EF \times ED}{BW \times AT} \times \left(\frac{R_{inhchildren} \times ED_{children}}{BW_{children}} \times \frac{R_{inhadults} \times ED_{adults}}{BW_{child}} \right) \quad \text{Eq. 7}$$

Since there are no standard reference values for RDS, the rates of inhalation and ingestion, and particle emission factor are those from the most similar studies in soil sciences. The estimated dose for each element via exposure is divided by the corresponding Reference Dose (RfD) to obtain a hazard quotient (HQ). A chronic RfD is an estimate of a daily exposure level for the human population, including sensitive subpopulations, that is likely to be without an appreciable risk of deleterious effects during a lifetime. Chronic RfDs are specifically developed to be protective for long-term exposure (from 7 years to a lifetime) to a compound. The hazard index (HI) is equal to the sum of all the HQ calculated by Equation 8.

$$HI = HQ_{ing} + HQ_{inh} + HQ_{dermal} = (D_{ing} / RfD_{ing}) + (D_{inh} / RfD_{inh}) + (D_{dermal} / RfD_{dermal}) \quad \text{Eq. 8}$$

Where, RfD_{ing} is the oral reference dose, mg kg^{-1} day^{-1}; RfD_{inh} is inhalation reference dose, mg kg^{-1} day^{-1}; RfD_{dermal} dermal reference dose, mg kg^{-1} day^{-1}.

This approach assumes that the magnitude of the adverse impact is proportional to the sum of the simultaneous subliminal exposure proportions to the acceptable exposure for each chemical product (USEPA, 1989). If $HI < 1$, there is no significant risk of non-carcinogenic effects. If $HI > 1$, then there is a possibility that non-carcinogenic effects occur, and get bigger the probability when the HI value increase (USEPA, 2001). Whereas for the carcinogenic effect, *LADD* is multiplied by the slope factor (*CSF*) to obtain the cancer risk level (*CR*) which is expressed by **Equation 9** (Zheng et al. 2010; Yang et al., 2013).

$$CR = LADD \times CSF \quad \text{Eq. 9}$$

It is considered an acceptable risk when the value of CR is lower than 1E-06 – 10-04E. The values of CSF and RfD for the tested metals are displayed in Table S2 according to the Risk Assessment Information System (RAIS) compilation of the

United States Department of the Energy (DOE) (Van der Berg 1994; Ferreira-Baptista and De Miguel 2005).

4.2.6. Geo- and multivariate analysis

The spatial distribution of metals was mapped by ArcGIS 10.1 using the Kriging interpolation method. Principal component analysis (PCA) which is one of the most classical source-receptor approaches was employed to qualitatively estimate the potential source apportionment of heavy metals and was computed by OriginPro 9 (OriginLab Corporation, US). Kruskal-Wallis H test was used to exam the influence of environmental factors on the spatial distribution of metals at a 0.05 significance level and was computed by SPSS 21.0 (SPSS Software, SPSS Inc., Chicago, IL). In addition, hierarchical cluster analysis (HCA) was further employed to identify the hidden patterns and interrelationships in the data matrix.

4.3. Results and discussion

4.3.1. Heavy metal pollution level assessment

As shown in Table 4.2., regardless of land-use type, Mn has the highest average concentration (194.0 ± 20.7 mg kg-1, mean ± standard error of the mean) among the given metals and followed by Zn (154.3 ± 21.3 mg kg-1) > Pb (141.5 ± 65.4 mg kg-1) > Cu (75.6 ± 24.3 mg kg-1) > Cr (21.3 ± 4.5 mg kg-1) > Ni (1.6 ± 0.3 mg kg-1) > Cd (0.1 ± 0.03 mg kg-1). Compared to the worldwide data shown in Table S3, generally, the average concentrations of certain metals were comparable with similar studies reporting ranges from 534 mg kg-1 (Tanner et al. 2008) to 42 mg kg-1 (Ferreira-Baptista and De Miguel, 2005) for Cu, 4024 mg kg-1 to 112 mg kg-1 (Cortés et al. 2017) for Zn, 666 mg kg-1 (Martínez & Poleto 2014) to 47 mg kg-1 (Charlesworth et al. 2003) for Pb, and 11 mg kg-1 (Saeedi et al. 2012) to 0.1 mg kg-1 (Cortés et al. 2017) for Cd. The average concentrations of the other metals were lower than the ranges from 1215 mg kg-1 (Saeedi et al. 2012) to 258 mg kg-1

(Ferreira-Baptista & De Miguel 2005) for Mn, 324 mg kg-1 (Tanner et al. 2008) to 26 mg kg-1 (Ferreira-Baptista & De Miguel 2005) for Cr, and 177 mg kg-1 (Rasmussen et al. 2001) to 16 mg kg-1 (Cortés et al. 2017) for Ni. Furthermore, the average concentrations of metals in this study were higher than the reference data such as Earth's crust, urban and rural soils (Table S3), but excluding Ni and Mn.

Pearson correlation analysis (Table S4) shows that the pairs of Ni-Cu, Ni-Cr, Ni-Mn, and Cr-Mn had relatively high Pearson's correlation coefficient of $r = 0.93$, 0.97, 0.95, and 0.92 respectively. These strong correlations could be attributed to the anthropogenic activities. All the pairs with Pb had moderate correlations ($P < 0.01$), which indicates alternative source contributors.

In terms of land-use type, generally, the highest mean concentrations of metals occurred at the commercial areas (and followed by residential > highway > GP areas) which were consistent with the other studies that the commercial area typically has an elevated heavy metal content (Kamani et al., 2015; Zhang et al. 2017). In the present study, the comparable higher values could be due to its various vehicle commercial activities of vehicles, such as retailing, repair, and installation of all vehicle parts, chemicals, equipment, and accessories, as well as a lack of waste management protocols. By contrast, the lowest average contents of metals were found in the GP area which was about 3-50 fold lower than in the commercial areas. The relative lower contents could be attributed to the non-commercial and non-industrial land-use functions of the government institutions and parks.

The spatial distribution of metals in RDS was further visualized in Figure 4.2. Two high-pollution hotspots were found at the commercial areas (northwest and southeast of the city). The concentrations of the given metals spatially decreased along commercial to residential gradient. Therefore, the heavy metal mitigation plan could be conducted especially in the commercial areas, e.g., an optimization of city street sweeping strategy with a higher frequency at the commercial area would be recommended to remove elevated hazardous materials.

Table 4.1 Parameters used for characterization exposure risk

Variable	Definition	Value	References
C	Specific concentrations of the metals in RDS samples		
IngR	Ingestion rate	200 mg day^{-1} for children and 100 mg day^{-1} for adults	USEPA, 2001
InhR	Inhalation rate	7.6 m^3 day^{-1} for children and 20 m^3 day^{-1} for adults	Van den Berg, 1994; Ferreira-Baptista and De Miguel, 2005
EF	Exposure frequency	350 day $year^{-1}$ for near street residential and outdoor workers	USEPA, 2001
ED	Exposure duration	6 years for children and 30 years for adults	USEPA, 2001
SA	Dermal exposure area	2800 cm^2 for children and 5700 cm^2 for adults	USEPA, 2001
SL	Skin adherence factor	0.2 mg cm^{-2} for children and 0.07 mg cm^{-2} for adults	USEPA, 2001
ABS	Dermal absorption factor	0.001 for all elements (unitless)	Ferreira-Baptista and De Miguel, 2005
PEF	Particle emission factor	1.36×10^9 m^3 kg^{-1}	USEPA, 2001
BW	Average body weight	15 kg for children and 70 kg for adults	USEPA, 2001
AT	Averaging time	ED×365 days for non-carcinogens	Ferreira-Baptista and De Miguel, 2005

Table 4.2 Descriptive statistics of metal concentrations and geo-accumulation index (Igeo)

Land use		**Concentrations in mg kg^{-1}**						
		Cd	Pb	Ni	Cu	Zn	Cr	Mn
Commercial (n = 8)	Mean	0.3	430.1	2.6	143.0	236.3	36.7	280.8
	Max	0.7	1188.6	8.2	624.5	481.9	124.6	642.9
	Min	0.01	20.5	1.0	11.1	61.9	9.4	147.6
	SD	0.3	541.3	2.4	205.8	147.6	39.5	159.2
	SEM	0.09	191.4	0.9	72.8	52.2	14.0	56.3
	I_{geo}	G0	G3	G0	G1	G2	G0	G0
Residential (n = 8)	Mean	0.08	23.5	1.0	49.3	140.1	12.5	161.9
	Max	0.3	51.1	1.7	258.1	313.3	20.0	248.0
	Min	0.01	12.4	0.6	10.4	0.8	6.2	105.7
	SD	0.09	11.9	0.3	84.7	91.7	4.2	50.6
	SEM	0.03	4.2	0.1	30.0	32.4	1.5	17.9
	I_{geo}	G0	G0	G0	G0	G0	G0	G0
Highway (n = 8)	Mean	0.04	20.7	1.3	47.7	118.1	18.7	164.1
	Max	0.1	40.7	2.1	149.2	226.3	30.6	237.3
	Min	0.01	9.1	0.9	19.8	70.8	10.8	121.8
	SD	0.04	12.9	0.4	42.1	51.3	6.5	38.6
	SEM	0.01	4.6	0.2	14.9	18.1	2.3	13.6

	I_{geo}	G0	G0	G0	G0	G1	G0	G0
GP	Mean	0.01	8.8	0.9	39.9	70.2	10.1	127.9
(n = 3)	Max	0.02	12.9	1.0	74.6	100.5	17.7	185.2
	Min	0.01	2.7	0.7	9.6	51.4	5.5	83.8
	SD	0.00	5.4	0.2	32.7	26.5	6.6	52.0
	SEM	0.002	3.1	0.1	18.9	15.3	3.8	30.0
	I_{geo}	G0	G0	G0	G0	G0	G0	G0
Overall	Mean	0.1	141.5	1.6	75.6	154.3	21.3	194.0
(n = 27)	Max	0.7	1188.6	8.2	624.5	481.9	124.6	642.9
	Min	0.01	2.7	0.65	9.6	0.79	5.5	83.8
	SD	0.1	339.7	1.5	126.1	110.6	23.5	107.4
	SEM	0.03	65.4	0.3	24.3	21.3	4.5	20.7
	I_{geo}	G0	G3	G0	G1	G1	G0	G0

4.3.2. Heavy metal risk assessment

4.3.2.1. Enrichment assessment derived from Igeo index

As given in Table 4.2, most of the studied land uses lay in the categories of uncontaminated (G0) excluding the commercial areas. Metals in the commercial areas lay in the categories from uncontaminated (G0) to highly contaminated (G3), especially due to the elevated contents of Pb (G3), Zn (G2), and Cu (G1).

4.3.2.2. Enrichment assessment derived from PLI index

A visualization enrichment map was performed based on the PLI index as shown in Figure 4.2. The mean PLI values of the given metals spatially decreased along commercial to residential gradient. The commercial areas have a mean PLI value of 1.8 and fall in the slight pollution corresponds to one of the categories proposed by Tomlinson et al. (1980), for the pollution Load Index (PLI). GP, residential, and highway areas lay in the non-pollution category. In other words, according to the PLI assessment, the pollution levels decreased from commercial to residential gradient.

4.3.2.3. Exposure health risk assessment

Following the Equation 4 - 9, the human health risk assessment of metals in RDS for adults and children through the three possible exposure routes were calculated and given in Figure 4.3 and Table S5. For the non-carcinogenic risk, the ingestion of RDS was identified as the main pathway via exposure of metals for adults and children followed by the dermic contact, which was consistent with the most similar studies (Ferreira-Baptista and De Miguel 2005, Liu et al., 2014; Li et al., 2016). In general, as given in Figure 4.3(a) and (b) both of the adults and children have the HI values with a safe level (< 1). In other words, there is no potential risk of carcinogenic effects and the potential risks decreased along commercial to residential gradient. However, the HI values for children were higher than them for

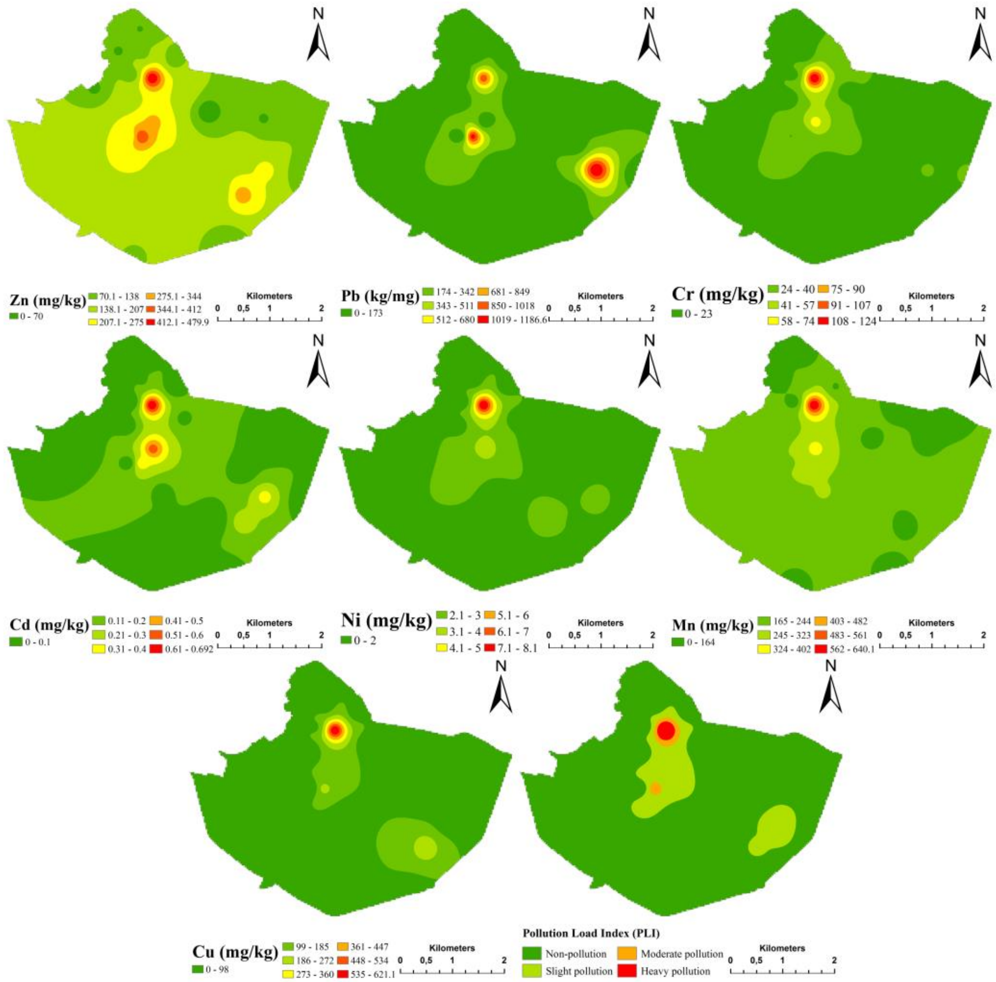

Figure 4.2 Spatial distribution of heavy metal concentrations in RDS samples and its pollution level derived from pollution load assessment (PLI)

adults. A lower body weight and a higher ingestion rate of the children could be attributed to the higher values of risk through ingestion and dermal contact respectively (Men et al., 2018). To reduce the potential risk to children, however, it is wise to promote good hygiene habits.

In terms of the given metals, the mean values of HI decreased in the following order: Cr > Cu > Pb > Zn > Cd > Ni. The HI values of Cr were about four times higher in average than the other metals. Table 4.3 displays the values of LADD and CR of Cr, Ni, and Cd via inhalation. Although Cr showed a higher risk than Ni and Cd, the carcinogenic risk of Cr was lower than the threshold value (1E-06 – 10-04E). However, it is important to address the attention to the possible health risk due to the exposure in the areas with higher metals' concentrations especially for children, street sweepers, public transportation drivers and the area inhabitants.

4.3.3. Hierarchical cluster analysis

A visible dendrogram classification derived by the hierarchical cluster analysis (HCA) was further employed to assess the effect of the influencing factors of land use and pavement roughness on the metals' concentration. The raw data was firstly standardized using z-score. Pearson correlation was used as a similarity measure, and the average agglomeration method was used to classify the cluster. According to the HCA results shown in Figure 4.4(a), all the metals were firstly formed together due to the similar nature characteristics. Then, the metals were linked to the pavement roughness suggesting surface roughness influenced the trapping of metals on the pavement surface. Finally, the metal concentrations were generally land-use dependent, however, compared with pavement roughness the influence of land-use on the distribution of metals was far lower.

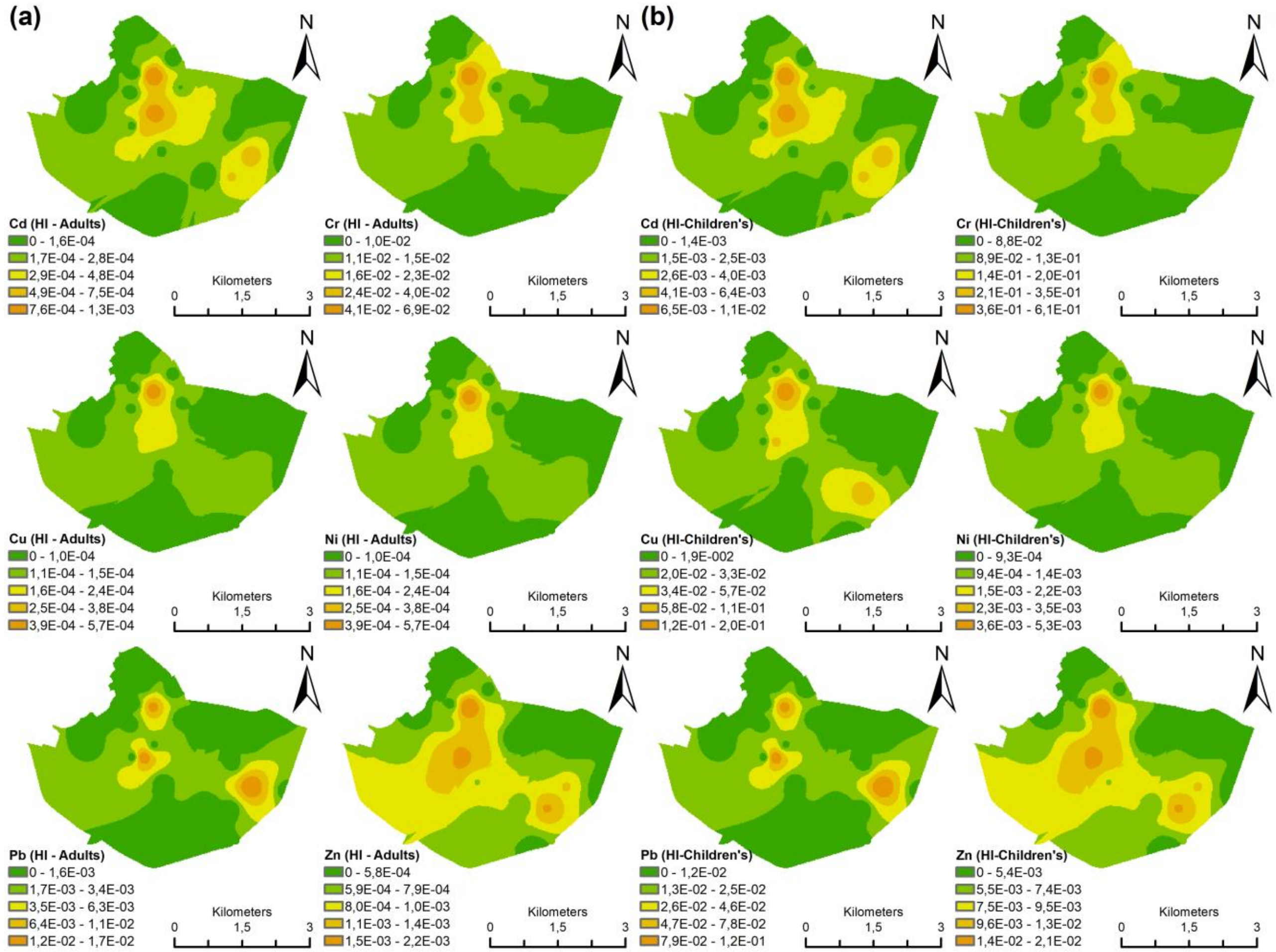

Figure 4.3 Exposure health risk assessment of metals in RDS derived from the hazard index for (a) adults and (b) children

T**able 4.3** Lifetime average daily dose and risk for each carcinogenic metal

Land use	Element	***LADD$_{inh}$* (mg kg^{-1} day^{-1})**	***CR***
GP	Cd	3.91E-12	2.46E-11
	Ni	2.44E-10	2.05E-10
	Cr	2.75E-09	1.16E-07
Commercial	Cd	7.27E-11	4.58E-10
	Ni	7.07E-10	5.94E-10
	Cr	1.00E-08	4.21E-07
Residential	Cd	2.18E-11	1.37E-10
	Ni	2.86E-10	2.40E-10
	Cr	3.41E-09	1.43E-07
Highway	Cd	1.03E-11	6.51E-11
	Ni	3.53E-10	2.97E-10
	Cr	5.12E-09	2.15E-07

Subsequent to the HCA analysis, the influence of land use on specific metals were further evaluated by the Kruskal-Wallis H test. Results show that there is no statistically significant difference in Cd, Cu, Zn, and Cr concentrations among the different land uses ($p > 0.05$). While a significant difference was found among Pb, Ni, and Mn concentrations ($p < 0.05$). It indicates that land use has a significant influence on the distribution of Pb, Ni, and Mn. Specifically, differences in Pb occurred between commercial and GP ($P = 0.006$), and commercial and highway areas ($P = 0.041$). Mn and Ni presented differences in commercial and GP ($P = 0.046$), and residential and commercial areas ($P = 0.045$), respectively.

4.3.4. Potential source identification

Since the variabilities among metals' correlation and content are mostly due to different sources contributors, a potential source identification was extracted by PCA receptor model. The purpose of PCA is to reduce the dimensionality of the original data matrix to a minimum number of principal components. Each principal component is a linear combination of the original variables. All the components are orthogonal to each other, and thus result in the smallest possible covariance (Zhang et al. 2013; Banerjee et al. 2015).

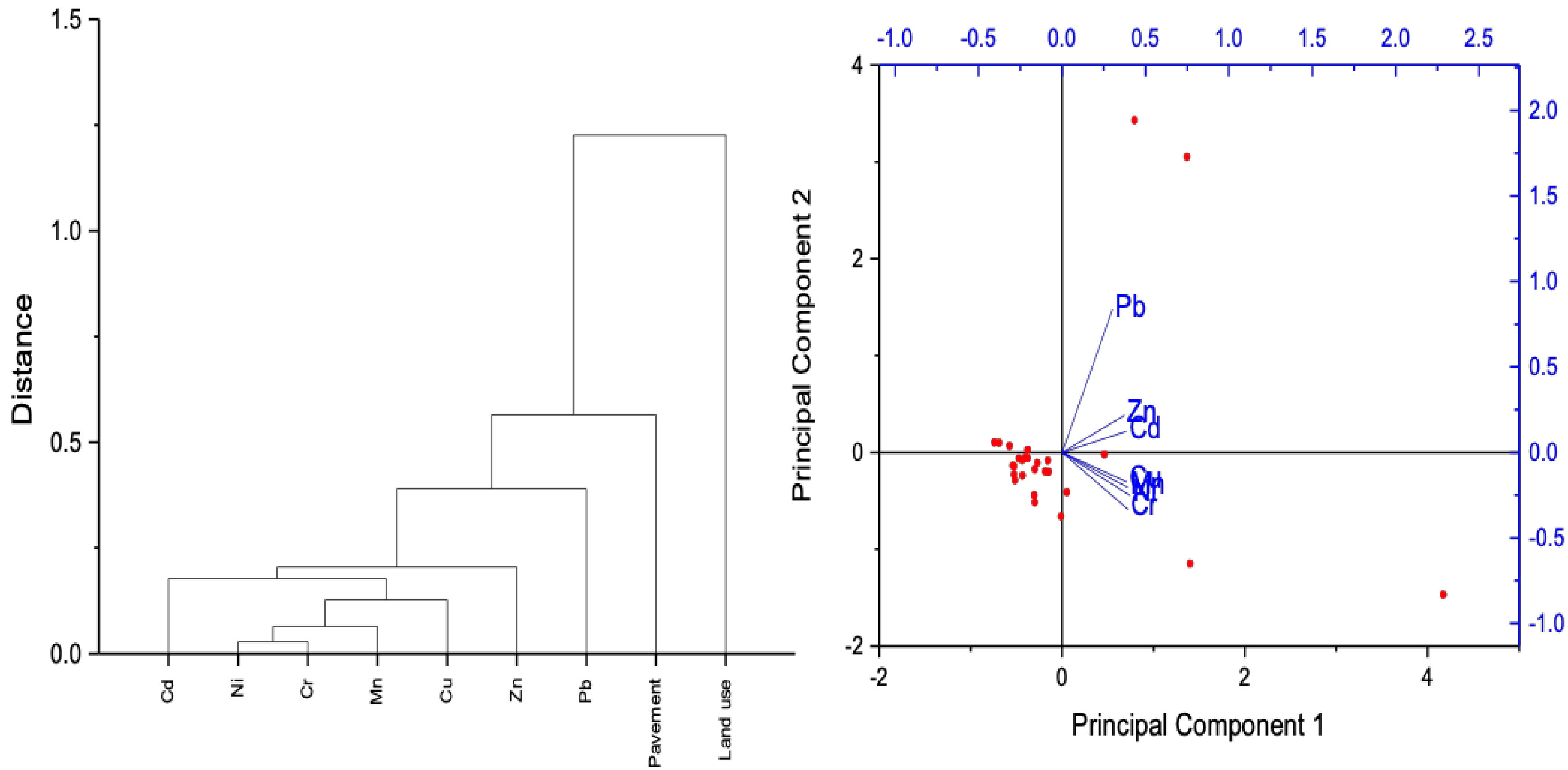

Figure. 4.4 (a) Dendrogram of hierarchical cluster analysis of given variables, and (b) PCA biplot obtained for metal contentes in RDS samples

According to the component matrix as given in Table 4.4 (a) and Figure 4.4(b), two principal components (potential sources) were extracted. The sum of the variances of the first two components exceeded 90 % of the total variance of the original data. The first component was responsible for 81.7 % of the total variance. This component was heavily dominated by nearly all of the given metals. There was no obvious source fingerprint recognizable from this component. In other words, no single source could represent the metal profiles in this component. More explicit, Ni, Cu, Cr, and Mn were highly weighted and to a lesser extent by Zn and Cd as given in Figure 4.4(b). In soil sciences, it has been reported that Ni, Cr, and Mn were commonly linked to the geochemical origin, such as parent rocks (Micó et al. 2006). Meanwhile, comparably high contents of Ni, Zn, and Cd in RDS samples were indicative of vehicular origin. In fact, Ni was found in the auto brake lining and tire tread (Loganathan et al. 2013). Zn is added as Zn oxide (ZnO) to the tire rubber as an activator to accelerate vulcanization when producing tires (Zhang et al. 2015b). Cu (CuO) is a component of brake pads with content up to 16% (Zhang et al. 2015b). Accordingly, this component was attributed to geochemical and vehicular sources.

The second component was responsible for 8.9 % of the total variance. This component was characterized by a high loading of Pb. The source apportionment of Pb is a complex issue. The main emission source of Pb used to be the combustion of leaded gasoline (Manno et al., 2006). The use of leaded gasoline gives a boost to the lead load especially in RDS even at the beginning of 21st century. For example, tetraethyl- and tetramethyl-lead were added to gasoline from the 1920s until the late 1990s. However, the gradual change to unleaded fuels leaves the question whether there is a current source of metal or these are accumulations from legacy Pb (Trujillo-González et al., 2016). A recent study in Colombia reported that the commercial paints still contain high levels of Pb (Silva et al., 2016). However, this, added to the historical use of leaded petrol, are possible sources

Table 4.4 Component coefficients matrix of heavy metals

Item	Component	
	1	**2**
Cd	0.38377	0.12252
Pb	0.30126	0.83315
Ni	0.40551	-0.25053
Cu	0.38628	-0.17212
Zn	0.37398	0.2158
Cr	0.39405	-0.33232
Mn	0.39138	-0.20361
Eigenvalue	5.72	0.63
% of Variance[a]	81.65	8.94
Cumulative %[b]	81.65	90.59
Potential source		

[a] The percentage of the total variability (initial eigenvalues) explained by each principal component.

[b] The amount of variance accounted for by each component.

4.4. Conclusions

This study focused on land use dependent spatial variation and exposure risk of metals in road-deposited sediment (RDS). Results show that commercial areas had the highest mean metals concentrations among the given land uses, and thereafter posed a higher exposure risk than the other land uses. Hierarchical cluster analysis reveals that surface roughness has a more direct influence than land use type on metals' distribution. Land use had a significant influence on the distribution of Pb, Ni, and Mn. The elevated metals contents could be attributed to the geochemical and vehicular sources, along with leaded petrol and paintings sources, which was identified by the principal component analysis. According to the exposure human health risk assessed by Hazard Index (HI), child has a higher health risk than adult due to the exposure to metals in RDS.

The data reported herein could facilitate the identification of pollution hotspots of metals in the urban areas and assist the potential source-oriented heavy metal mitigation. A land-use dependent city surface sweeping strategy could be planned and optimized to reduce the potential exposure health risk. The reference data provided here would be useful to the governmental stakeholder for the environmental management and urban planning of a medium-sized city.

4.5. Acknowledgment

The authors acknowledge the financial support provided by the Dirección General de Investigaciones DGI of the Universidad de los Llanos, within the framework of project CO1-F02-018-2016 "*Hot-spots o zonas riesgo por la presencia de metales pesados en sedimentos viales en la ciudad de Villavicencio*" and to the staff of the Instituto de Ciencias Ambientales de la Orinoquia Colombiana-ICAOC. Jin Zhang acknowledges the financial support by COLABIS project (Collaborative Early Warning Information Systems for Urban Infrastructures, Grant No.: 03G0852A) funded by German Federal Ministry of Education and Research (BMBF). Mention of trade names or commercial products does not constitute endorsement or recommendation for use. This manuscript has not been subjected to the above agencies' required peer and policy review and therefore does not reflect the views of the above agencies and no official endorsement should be inferred.

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4.7. Supplementary Material

Land use dependent spatial variation and exposure risk of heavy metals in road-deposited sediment in Villavicencio, Colombia

Table S 1 Characteristics of the sampling areas

Land use	Predominant activity	Pavement roughness	Traffic load	Type of vehicles
Commercial	Automotive mechanic services, and auto parts sales	Bad to Medium	Medium	Private, heavy traffic, and public transport, Urban transport
Residential	Housing, educational centers, and restaurants	Good to Medium	Low	Private, and public transport
Highway	Vehicle transit	Good	High	Heavy traffic, private, public and intercity transport
GP	Government institutions, and parks	Good	Low	Private, and public transport

Table S 2 Reference dose (RfD) and cancer slope factor (CSF) via exposure for each non-carcinogenic metal (Cr, Ni, and Cd) (Ferreira-Baptista and Miguel, 2005; US EPA, 2011)

	Cr	**Ni**	**Cu**	**Zn**	**Cd**	**Pb**
R*f*D$_{ing}$	3.00E-03	2.00E-02	4.00E-02	3.00E-01	1.00E-03	3.50E-01
R*f*D$_{inh}$	2.86E-05	2.06E-02	4.02E-02	3.00E-01	1.00E-03	3.52E-03
R*f*D$_{dermal}$	6.00E-05	5.40E-03	1.20E-02	6.00E-02	1.00E-05	5.25E-04
C*S*F$_{inh}$	42.0	0.84	-	-	6.30	-

Note: *RfD* and *CSF* (mg kg^{-1} day^{-1})

Table S 3 The reviewed global metal concentration in RDS and standard guidelineesta tabvla es muy Buena y hay que ampliarla

Study area		Heavy metal concentrations in mg kg^{-1} of dry mass							Number of samples	Sample type	Year
		Cd	Pb	Ni	Cu	Zn	Cr	Mn			
Present											
	Villavicencio, Colombia										
		0.1	141.5	1.6	75.6	154.3	21.3	194.0	27	Road deposited sediment	2017
Africa											
	Luanda, Angola (Ferreira-Baptista and De Miguel, 2005)	1.1	351	10	42	317	26	258	92	Road deposited sediment	2005
Asia											
	Tehran, Iran (Saeedi *et al.* 2012)	10.7	257.4	34.8	225.3	873.2		1214.5	50	Road deposited sediment	2012
	Beijing, China (Wei *et al.* 2015)	0.72	105	25.2	69.9	222	84.7	n/a	154	Road deposited sediment	2015
	Shanghai, China (Shi *et al.* 2008)	1	237	66	258	753	264	n/a		Road deposited sediment	2008
	Guangzhou, China (Huang *et al.* 2014)	2.14	388	41.4	192	1777	176	n/a	30	Road deposited sediment	2010
	Hong Kong, China (Tanner *et al.* 2008)	1.8	240	n/a	534	4024	324	n/a		Road deposited sediment	2005
	Nanjing, China (Hu *et al.* 2011)	1.1	103	55.9	123	394	126	n/a	35	Road deposited sediment	2009
	Chengdu, China (Li *et al.* 2017)	1.66	82.3	24.4	100	296	84.3	n/a	75	Road deposited sediment	2016
	Xi'an, China	n/a	231	16	95	421	167	n/a			

	(Yongming *et al.* 2006)										
	Baoji, China (Lu *et al.* 2009)	n/a	433	48.8	123	715	127	n/a			
	Amman, Jordan (Al-Khashman 2007)	1.7	236	88	177	258	n/a	n/a	120	Road deposited sediment	2007
	Tumpat, Malaysia (Sow *et al.* 2013)	2.88	181.3	35.12	262.17	274.92	n/a	n/a	20	paddy field soils	2011
	Islamabad, Pakistan (Faiz *et al.*, 2009)	5	104	23	52	116	n/a	n/a	13	Road deposited sediment	2009
Europe											
	Istanbul, Turkey (Sezgin *et al.* 2004)	4.3	240.5	37.75	91.77	271.95	n/a	n/a	22	Road deposited sediment	2003
	Birmingham, UK (Charlesworth *et al.*, 2003)	1.62	48	41.1	466.9	534	n/a	n/a	100	Road deposited sediment	2003
	Coventry (Charlesworth *et al.* 2003)	0.9	47.1	129.7	226.4	385.7	n/a	n/a	100	Road deposited sediment	2003
	Oslo, Norway (Miguel *et al.*, 1997)	1.4	180	41	123	412	n/a	833	224	Road deposited sediment	1997
	Madrid, Spain (Miguel *et al.*, 1997)	n/a	1927	44	188	476	61	362	<224	Road deposited sediment	1997
	Bilbo, Spain (Carrero *et al.*, 2013)	0.1	22	21	15	60	38	n/a	n/a	Roadside soil	2013
	Naples, Italy (Imperato *et al.*, 2003)	n/a	262		74	251	11	n/a	173	Urban soils	1999

	Kavalla, Greece (Christoforidis and Stamatis, 2009)	0.2	301	58	124	272		n/a	96	Road deposited sediment and roadside soil	2009
South America and Latin America											
	Porto Alegre, Brazil (Martínez & Poleto 2014)	1.5	145.6	57	n/a	723.6	n/a	n/a	8	Residential	2014
		0.4	139.4	61.5	n/a	491	n/a	n/a	n/a	Industrial	
		2.2	665.6	93	n/a	744.2	n/a	n/a	n/a	Commercial	
North America											
	Ensenada, Baja California, Mexico (Cortés *et al.* 2017)	n/a	55	15.8	40.4	111.8	45.6	n/a	86	Road deposited sediment	2017
	Tijuana, Mexico Quiñonez-Plaza et al. (2017)	0.1	31.8	n/a	50.2	n/a	17.1	n/a	30	Road deposited sediment	2017
	Massachusetts, USA (Apeagyei *et al.*, 2011)	n/a	73	n/a	105	240	n/a	456	85	Road deposited sediment	2011
	Hawaii, USA (Sutherland and Tolosa, 2000)	n/a	106	177	167	434	273	1035	13	Road deposited sediment	1999
		n/a	13	303	114	132	507	1613	n/a	Background soil	
	Ottawa, Canada (Rasmussen *et al.* 2001)	0.37	39.05	15.2	65.84	112.5	n/a	431.5	50	indoor dust and exterior soil	2001
Standard reference values											

	Earth' crust (Taylor and McLennan, 1995)	0.1	5×10^{-4}	20	25	71	35	600	n/a	Earth' crust	1995
	PC_{soil} (MEP, 1996)	0.6	350	60	100	300	350		n/a	Soil	1996

Table S 4 Pearson's correlation coefficient between heavy metals in road-deposited sediment samples (n = 27)

		Cd	Pb	Ni	Cu	Cr	Zn	Mn
Cd	Pearson	1.00	0.685**	0.842**	0.789**	0.845**	0.817**	0.813**
	Sig. (bilateral)		0.000	0.000	0.000	0.000	0.000	0.000
Pb	Pearson	0.685**	1.00	0.592**	0.575**	0.530**	0.684**	0.589**
	Sig. (bilateral)	0.000		0.001	0.002	0.004	0.000	0.001
Ni	Pearson	0.842**	0.592**	1.00	0.925**	0.972**	0.800**	0.948**
	Sig. (bilateral)	0.000	0.001		0.000	0.000	0.000	0.000
Cu	Pearson	0.789**	0.575**	0.925**	1.00	0.877**	0.820**	0.812**
	Sig. (bilateral)	0.000	0.002	0.000		0.000	0.000	0.000
Cr	Pearson	0.845**	0.530**	0.972**	0.877**	1.00	0.749**	0.923**
	Sig. (bilateral)	0.000	0.004	0.000	0.000		0.000	0.000
Zn	Pearson	0.817**	0.684**	0.800**	0.820**	0.749**	1.00	0.787**
	Sig. (bilateral)	0.000	0.000	0.000	0.000	0.000		0.000
Mn	Pearson	0.813**	0.589**	0.948**	0.812**	0.923**	0.787**	1.00
	Sig. (bilateral)	0.000	0.001	0.000	0.000	0.000	0.000	
****Correlation is significant at the 0.01 level (bilateral).**								

Table S 5 Non-carcinogenic risk Hazard Quotient exposure pathway and Hazard Index average daily dose for each element ADD: Average Daily Dose (mg kg-1 day-1). HQ: Hazard Quotient (unitless). HI: Hazard Index (unitless)

Land use	Element	Adults								Children						
		D_{ing}	D_{inh}	D_{der}	HQ_{ing}	HQ_{inh}	HQ_{der}	HI		D_{ing}	D_{inh}	D_{der}	HQ_{ing}	HQ_{inh}	HQ_{der}	**HI**
GP	Cd	1.96E-08	2.89E-12	7.83E-11	1.96E-05	2.89E-09	7.83E-06	2.75E-05		1.83E-07	5.12E-12	5.13E-10	1.83E-04	5.12E-09	5.13E-05	**2.35E-04**
	Pb	1.21E-05	1.78E-09	4.83E-08	3.46E-05	5.05E-07	9.19E-05	1.27E-04		1.13E-04	3.15E-09	3.16E-07	3.23E-04	8.96E-07	6.02E-04	**9.26E-04**
	Ni	1.22E-06	1.80E-10	4.88E-09	6.12E-05	8.74E-09	9.04E-07	6.21E-05		1.14E-05	3.19E-10	3.20E-08	5.71E-04	1.55E-08	5.92E-06	**5.77E-04**
	Cu	5.46E-05	8.03E-09	2.18E-07	1.37E-03	2.00E-07	1.82E-05	1.38E-03		5.10E-04	1.42E-08	1.43E-06	1.27E-02	3.54E-07	1.19E-04	**1.29E-02**
	Zn	9.61E-05	1.41E-08	3.84E-07	3.20E-04	4.71E-08	6.39E-06	3.27E-04		8.97E-04	2.51E-08	2.51E-06	2.99E-03	8.36E-08	4.19E-05	**3.03E-03**
	Cr	1.38E-05	2.03E-09	5.51E-08	4.61E-03	7.11E-05	9.19E-04	5.60E-03		1.29E-04	3.60E-09	3.61E-07	4.30E-02	1.26E-04	6.02E-03	**4.91E-02**
Commercial	Cd	3.65E-07	5.37E-11	1.46E-09	3.65E-04	5.37E-08	1.46E-04	5.11E-04		3.41E-06	9.52E-11	9.54E-09	3.41E-03	9.52E-08	9.54E-04	**4.36E-03**
	Pb	5.89E-04	8.66E-08	2.35E-06	1.68E-03	2.46E-05	4.48E-03	6.19E-03		5.50E-03	1.54E-07	1.54E-05	1.57E-02	4.36E-05	2.93E-02	**4.51E-02**
	Ni	3.55E-06	5.22E-10	1.42E-08	1.78E-04	2.53E-08	2.62E-06	1.80E-04		3.31E-05	9.26E-10	9.28E-08	1.66E-03	4.49E-08	1.72E-05	**1.67E-03**
	Cu	1.96E-04	2.88E-08	7.82E-07	4.90E-03	7.17E-07	6.51E-05	4.96E-03		1.83E-03	5.11E-08	5.12E-06	4.57E-02	1.27E-06	4.27E-04	**4.61E-02**
	Zn	3.24E-04	4.76E-08	1.29E-06	1.08E-03	1.59E-07	2.15E-05	1.10E-03		3.02E-03	8.44E-08	8.46E-06	1.01E-02	2.81E-07	1.41E-04	**1.02E-02**

	Cr	5.03E-05	7.40E-09	2.01E-07	1.68E-02	2.59E-04	3.35E-03	2.04E-02		4.70E-04	1.31E-08	1.32E-06	1.57E-01	4.59E-04	2.19E-02	**1.79E-01**
Residential	Cd	1.09E-07	1.61E-11	4.37E-10	1.09E-04	1.61E-08	4.37E-05	1.53E-04		1.02E-06	2.85E-11	2.86E-09	1.02E-03	2.85E-08	2.86E-04	**1.31E-03**
	Pb	3.22E-05	4.73E-09	1.28E-07	9.19E-05	1.34E-06	2.44E-04	3.38E-04		3.00E-04	8.39E-09	8.41E-07	8.58E-04	2.38E-06	1.60E-03	**2.46E-03**
	Ni	1.43E-06	2.11E-10	5.72E-09	7.17E-05	1.02E-08	1.06E-06	7.27E-05		1.34E-05	3.74E-10	3.75E-08	6.69E-04	1.81E-08	6.94E-06	**6.76E-04**
	Cu	6.76E-05	9.94E-09	2.70E-07	1.69E-03	2.47E-07	2.25E-05	1.71E-03		6.31E-04	1.76E-08	1.77E-06	1.58E-02	4.38E-07	1.47E-04	**1.59E-02**
	Zn	1.92E-04	2.82E-08	7.66E-07	6.40E-04	9.41E-08	1.28E-05	6.53E-04		1.79E-03	5.01E-08	5.02E-06	5.97E-03	1.67E-07	8.36E-05	**6.06E-03**
	Cr	1.71E-05	2.51E-09	6.82E-08	5.70E-03	8.79E-05	1.14E-03	6.92E-03		1.60E-04	4.46E-09	4.47E-07	5.32E-02	1.56E-04	7.45E-03	**6.08E-02**
Highway	Cd	5.19E-08	7.63E-12	2.07E-10	5.19E-05	7.63E-09	2.07E-05	7.26E-05		4.84E-07	1.35E-11	1.36E-09	4.84E-04	1.35E-08	1.36E-04	**6.20E-04**
	Pb	2.84E-05	4.18E-09	1.13E-07	8.11E-05	1.19E-06	2.16E-04	2.98E-04		2.65E-04	7.41E-09	7.42E-07	7.57E-04	2.10E-06	1.41E-03	**2.17E-03**
	Ni	1.77E-06	2.61E-10	7.08E-09	8.87E-05	1.27E-08	1.31E-06	9.00E-05		1.66E-05	4.63E-10	4.64E-08	8.28E-04	2.25E-08	8.59E-06	**8.37E-04**
	Cu	6.54E-05	9.61E-09	2.61E-07	1.63E-03	2.39E-07	2.17E-05	1.66E-03		6.10E-04	1.70E-08	1.71E-06	1.52E-02	4.24E-07	1.42E-04	**1.54E-02**
	Zn	1.62E-04	2.38E-08	6.46E-07	5.39E-04	7.93E-08	1.08E-05	5.50E-04		1.51E-03	4.22E-08	4.23E-06	5.03E-03	1.41E-07	7.05E-05	**5.10E-03**
	Cr	2.57E-05	3.78E-09	1.02E-07	8.56E-03	1.32E-04	1.71E-03	1.04E-02		2.40E-04	6.70E-09	6.71E-07	7.99E-02	2.34E-04	1.12E-02	**9.13E-02**

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5. IMPACT OF POTENTIALLY CONTAMINATED RIVER WATER ON AGRICULTURAL IRRIGATED SOILS IN AN EQUATORIAL CLIMATE

agriculture

MDPI

Article

Impact of Potentially Contaminated River Water on Agricultural Irrigated Soils in an Equatorial Climate

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Academic Editors: Rabin Bhattarai and Paul Davidson

Received: 6 April 2017; Accepted: 21 June 2017; Published: 24 June 2017

Abstract: Globally, it is estimated that 20 million hectares of arable land are irrigated with water that contains residual contributions from domestic liquids. This potentially poses risks to public health and ecosystems, especially due to heavy metals, which are considered dangerous because of their potential toxicity and persistence in the environment. The Villavicencio region (Colombia) is an equatorial area where rainfall (near 3000 mm/year) and temperature (average 25.6 °C) are high. Soil processes in tropical conditions are fast and react quickly to changing conditions. Soil properties from agricultural fields irrigated with river water polluted by a variety of sources were analysed and compared to non-irrigated control soils. In this study, no physico-chemical alterations were found that gave evidence of a change due to the constant use of river water that contained wastes. This fact may be associated with the climatic factors (temperature and precipitation), which contribute to fast degradation of organic matter and nutrient and contaminants (such as heavy metals) leaching, or to dilution of wastes by the river.

Keywords: trace elements; equatorial area; agricultural land use; wastewater irrigation

1. Introduction

The role of equatorial regions of the world in global food production is increasing [1]. Management of resources to produce more food in a sustainable manner has become increasingly important [2,3]. Anthropogenic contamination of soils by sewage and industrial chemicals has become a major source of concern. The input of toxic levels of trace elements into soils has occurred as a result of the use of agricultural chemicals [4] and sewage water for irrigation [5,6]. The productive use of wastewater has increased, as millions of small-scale farmers in urban and peri-urban areas of developing countries depend on wastewater or water sources, such as rivers, contaminated with wastewater to irrigate high-value edible crops for urban markets, often because they have no alternative sources of irrigation water. Undesirable constituents in wastewater can harm human health and the environment [7,8]. Proper use of wastewater with appropriate pretreatments can improve soil health without risking human health, but those pretreatments do not happen in many instances [9,10].

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Abstract

Globally, it is estimated that 20 million hectares of arable land are irrigated with water that contains residual contributions from domestic liquids. This potentially poses risks to public health and ecosystems, especially due to heavy metals, which are considered dangerous because of their potential toxicity and persistence in the environment. The Villavicencio region (Colombia) is an equatorial area where rainfall (near 3000 mm/year) and temperature (average 25.6 °C) are high. Soil processes in tropical conditions are fast and react quickly to changing conditions. Soil properties from agricultural fields irrigated with river water polluted by a variety of sources were analysed and compared to non-irrigated control soils. In this study, no physico-chemical alterations were found that gave evidence of a change due to the constant use of river water that contained wastes. This fact may be associated with the climatic factors (temperature and precipitation), which contribute to fast degradation of organic matter and nutrient and contaminants (such as heavy metals) leaching, or to dilution of wastes by the river.

5.1 Introduction

The role of equatorial regions of the world in global food production is increasing (Boul, 2009). Management of resources to produce more food in a sustainable manner has become increasingly important (Brevik et al., 2016; Keestra et al., 2016). Anthropogenic contamination of soils by sewage and industrial chemicals has become a major source of concern. The input of toxic levels of trace elements into soils has occurred as a result of the use of agricultural chemicals (Czarnecki and Düring, 2015) and sewage water for irrigation (Singh et al., 2010; Vergine et al., 2017). The productive use of wastewater has increased, as millions of small-scale farmers in urban and peri-urban areas of developing countries depend on wastewater or water sources, such as rivers, contaminated with wastewater to irrigate high-value edible crops for urban markets, often because they have no alternative sources of irrigation water. Undesirable constituents in wastewater can harm human health and the environment (Helmke and Losco, 2012; Qadir et al., 2010). Proper use of wastewater with appropriate pretreatments can improve soil health without risking human health, but those pretreatments do not happen in many instances (Becerra-Castro et al., 2015; Gatta and Libutti, 2016).

The dumping of domestic and industrial municipal wastewater dates back 400 years and is now a common practice in many parts of the world (Reed et al., 1995). It is estimated that 20 million hectares of arable land globally are irrigated with water with residual contributions from domestic liquids without treatment or with inadequate treatment (Aydin et al., 2015; Fatta-Kassinos et al., 2011; Wuana and Okineimen, 2011). This poses risks to public health and ecosystems, especially due to the content of heavy metals, considered dangerous because of their potential toxicity and persistence in the environment (Alobaidy et al., 2010; Mapanda et al., 2005; Qadir et al., 2015). Also, the ability to reduce fertilizer inputs due to the nutrient content of wastewater motivates farmers to use these waters to irrigate crops, and the application to cropland is often seen as being an environmentally acceptable disposal method for effluents (Aydin et al., 2015; Fatta-Kassinos et al., 2011; Kim et al., 2015). Positive effects on soil biodiversity following wastewater application have also been reported (Disciglio et al., 2015).

Heavy metals and trace elements in the soil system are issues that are of specific interest as they fall into two categories (Brevik and Sauer, 2015; Rahman et al., 2012). Metals such as copper (Cu), zinc (Zn), manganese (Mn), iron (Fe), and molybdenum (Mo) have been identified as essential micronutrients for plant growth, while cadmium (Cd), lead (Pb), chromium (Cr6+), nickel (Ni), mercury (Hg) and arsenic (As), besides not being essential to plants, have toxic effects even at very low concentrations (Pulido et al., 2013; Simmos et al., 2010). The accumulation of heavy metals in agricultural soils can affect the food chain by being transferred from soil to plant to humans, with the potential to negatively affect human health (Gupta et al., 2010). The levels of heavy metals in soils vary between regions and depend on factors including the parent material, application of fertilizers containing traces of these elements (Singh et al., 2010; Wang and Zang, 2014), and other factors such topography. The concentrations of heavy metals in wastewater are low, but prolonged use increases the possibility of accumulation of contamination in soil and groundwater, and transfer of those pollutants to plants (Abdu et al., 2011; Rattan et al., 2005). Wastewater may contain residues of industrial or domestic origin as well as urban runoff (Alobaidy et al., 2010; Trujillo-González et al., 2016). Guénon et al. (2016) reported that, in untreated wastewater, concentrations of Pb and methylmercury can reach 0.16 ± 0.05 mg/L and 3.8 ± 2.5 ng/L, respectively. Recently, technologies such as biochar have been proposed to phytostabilize contaminants in the soil and could potentially sequester contaminates and convert soils degraded by contamination into productive ecosystems once again (Gronwwald et al., 2015; Mahmoud and Abd, 2015; Paz-Ferreiro et al., 2014).

In this regard, the continued use of wastewater potentially threatens soil resources traditionally used to support food production (FAO-ISRIC-ISSS, 2006), as well as many other human activities. Soil is a dynamic entity serving five major biophysical functions: nutrient cycling; water retention; biodiversity and habitat; storage, filtering, buffering and transformation of compounds; and physical stability and support (Blum, 1993), all essential for the development of societies and for the determination of environmental quality functions (Koch et al., 2013; Pla, 2014). However, due to population growth, especially in developing counties, demand for goods and services have increased, and inadequate farming practices became factors that drove soil degradation and declines in soil C and nutrient concentrations (Barbero-Sierra et al., 2015; Pla, 2014; Xie et al., 2015). To counteract the negative effect of land degradation due to pollution in peri-urban irrigated agricultural areas, monitoring programs need to be stablished for agricultural practices in peri-urban areas that use water contaminated from domestic and industrial waste for irrigation to assess the impact of the contaminated water use on the functioning of soil. In addition, there is a need to develop measures to promote soil conservation and/or remediation, especially in developing regions, where there is a lack of treatment systems for domestic wastewater and storm water, and where industrial activity is high (Arora et al., 2008).

Although studies have been published on the use of contaminated water in agriculture in developing countries such as India and Zimbabwe (Cao and Hu, 2000; Mapanda et al., 2015; Nyamngaera and Mzezawa, 2008; Singh et al., 2004), there is little published data from Latin American developing countries. There is also little data for equatorial areas where rainfall exceeds 3000 mm/year, even though these areas are important for food production. One example of such an agricultural area is the region around the city of Villavicencio in Colombia.

A systematic study was conducted on the effect of river water contaminated by a variety of sources on soil pollution levels in the Villavicencio equatorial region. In this study, the impact of the use of contaminated river water for irrigation on the levels of trace elements in the soils in the area was assessed. The objectives of the present study were: (1) to identify the different sources of pollutants in the Ocoa river, the main water source running through the urban area of the city of Villavicencio; and (2) analyze the physico-chemical properties of agricultural soils irrigated with potentially contaminated water to create an effective scientific tool that assists decision makers in their attempts to preserve public health and conserve natural resources.

5.2. Materials and methods

5.2.1. Study Area

The study site is in the Villavicencio region (4°7′30″ N, 73°16′30″ W), located in the east center portion of Colombia (Figure 5.1). The area is characterized by high average annual rainfall (2888.8 mm; weather Station La Libertad-Code 35025020-IDEAM) with an average annual temperature of 25.7 °C and plain topography at an elevation of 243 m. This study was conducted in agricultural land irrigated with water from the Ocoa River, which includes effluents from different sources. Irrigation was applied during months that had a low supply of rainwater. Rainfall in the region is largely determined by the intertropical convergence zone, with a single mode regime where the months of April, May, June, July and October have the highest rainfall with values ranging from 305.8 to 431.6 mm/month and the dry season occurs in the months of December, January, February and March with rainfall ranging between 25.1 and 147 mm/month; the climatic classification of the region corresponds to tropical rainforest (IGAC, 2004). Soils in the study area are dominated by Inceptisols and Oxisols according to Soil Taxonomy (2006). These often translate into Cambisols or Ferralsols in the system of the FAO-ISRIC-ISSS (2006).

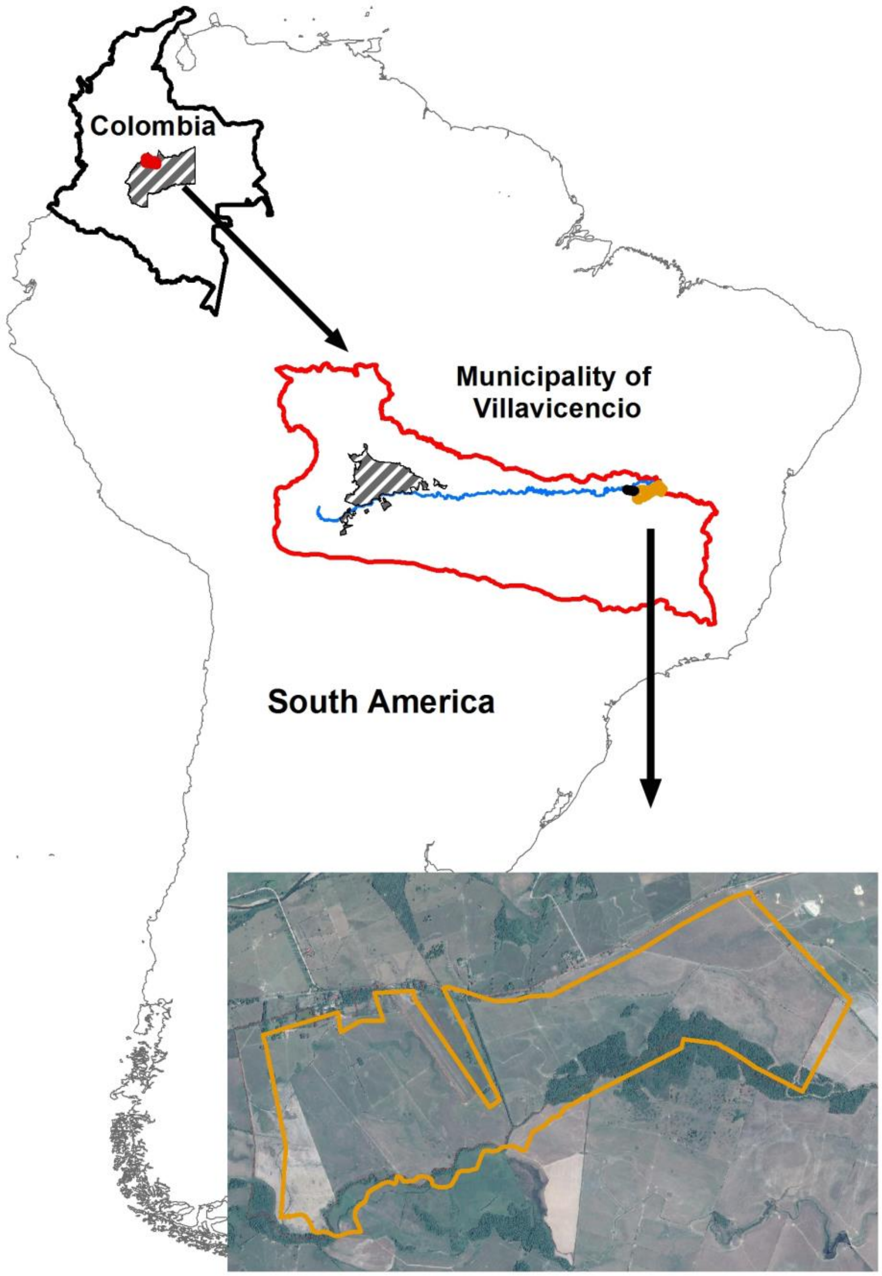

Figure 5.1 Geographical location of the study area. The red area in the Colombia map shows the Municipality of Villavicencio within the department of Meta (stripped pattern), the red outlined area in the middle map shows the municipality with urbanized areas in a stripped pattern and the study are in yellow, and the lower aerial photograph shows the studied fields in detail

The primary crop at the study site was rice (Oryza sativa) with occasional maize (Zea mays) for at least 25 years prior to 2014. A flood irrigation system was used with channels that allowed irrigation water to enter the field at the rate of 150 L min−1. In 2014, most of the study site (total of 540 ha) was converted to pastures for cattle grazing (420 ha), with only a small amount of rice production (120 ha) on the remaining area. The irrigation channels were still maintained and irrigation applied as needed. Soil samples for this study were collected in 2015.

5.2.2. Sources of Pollutants in the River Water

The identification of sources of pollution into the Ocoa River was done in several ways, including: field trips to find areas of effluent release, interviews with residents, photographic records, and geo-referencing (using a Global Positioning System -GPS Garmin 62SC). Points where numerous releases into the river were found were referred to as common outlet zones.

5.2.3. Soil Sampling

A total of 21 samples of agricultural land irrigated with contaminated water and 4 reference samples, or controls, in non-irrigated fields were taken in the agricultural area of interest at a depth of 0–30 cm (Micó et al., 2006). There are no crops in the area irrigated with freshwater (water that does not receive contamination inputs); therefore, it was not possible to establish a control that received irrigation with non-contaminated water. Sampling was done in a systematic cross, i.e., each of the sampling points were at uniform distances from each other, covering the entire area. Each sample consisted of five sub-samples and the sampling points were located using a GPS (Garmin 62 SC) and put into ArcGis 10.1 software (Esri, Redlands, CA, USA).

5.2.4. Laboratory Analysis

The determination of the total concentrations of heavy metals in soil (Cu, Zn, Ni, Pb, Cd) was performed by digestion in nitric acid, hydrochloric acid and hydrogen peroxide and atomic absorption spectrophotometry flame (Air-Acetylene, Environmental Protection Agency -EPA 3050B, 3111B SM). The pH was measured with a potentiometer in a 1:1 soil:water mix; the organic matter (OM) was determined by the Walkley–Black method (IGAC, 2006); available phosphorus by Bray II [45]; exchangeable bases (Ca, Mg, Na, K) by extraction with ethyl ammonium normal (pH 7.0) (IGAC, 2006); Ca and Mg were quantified by atomic absorption (IGAC, 2006); Na and K by atomic absorption spectrophotometry (IGAC, 2006), and textural analysis by sieve and hydrometer (IGAC, 2006). For quality control, blank samples were analyzed after every ten samples. All chemicals and solutions were of analytical standard book-reagent grade. Lastly, the quality was assured by using duplicates.

5.2.5. Statistical Methods and Isoline Plotting

Data were analyzed with descriptive statistics including mean (Me), standard deviation (SD), and coefficient of variation (CV) and also underwent a two-tailed Student t-test ($p = 0.05$) for mean differences. The spatial distribution of metals was represented by Kriging interpolation using ArcGIS software version 10.1.

5.3. Results and discussion

5.3.1. Sources of Pollutants in the River Water

Fifty-four points were identified along the Ocoa River over a distance of 69 km where domestic, agricultural and industrial wastes were dumped (Figure 5.2). Only 15 (28%) of these were authorized for dumping liquid waste, while for the remaining 39 (72%) it was not possible to establish that they had authorization from the environmental authority. However, in neither of the two scenarios was treatment for the remediation of wastewater done, which illustrates the problem mentioned by UN Water 2008), which states that developing countries do not treat about 90% of their liquid wastes. It was also found that 79% of the discharge points along the Ocoa River corresponded to domestic sources that were “common areas of domestic dumping” of numerous effluents. This is a common problem in all developing countries where the main problem of water pollution is due to the lack of basic sanitation, and is related to vulnerable sectors of the population that have no options other than polluted rivers as a source for the water they need to conduct essential life functions such as food preparation, personal hygiene, laundry, recreation and sewage services (chaggu et al., 2002; Qadir et al., 2010). In the municipality of Villavicencio Colombia, domestic sewage (79% of discharge sites) is concentrated and taken to points of discharge without treatment; however, not all homes are connected to the sewer system, because they have septic systems or simply pour wastes directly into a river. It was found that 17% of discharge points into the Ocoa River consisted of domestic effluent that was mixed with urban runoff, including agribusiness and car wash effluent. Industrial activity leading to hydrocarbon production accounted for 2% of the sources of pollution, and according to Ecopetrol (2014), organic and inorganic compounds in the wastewater discharged to the Ocoa River remain below levels stipulated by Colombian environmental standards. The last contribution found (2%) was related to a closed municipal landfill, which according to authors like Krook et al. (2012) and Abu-Daabes et al., (2013), generated atmospheric emissions and leachates containing organic and inorganic components including heavy metals.

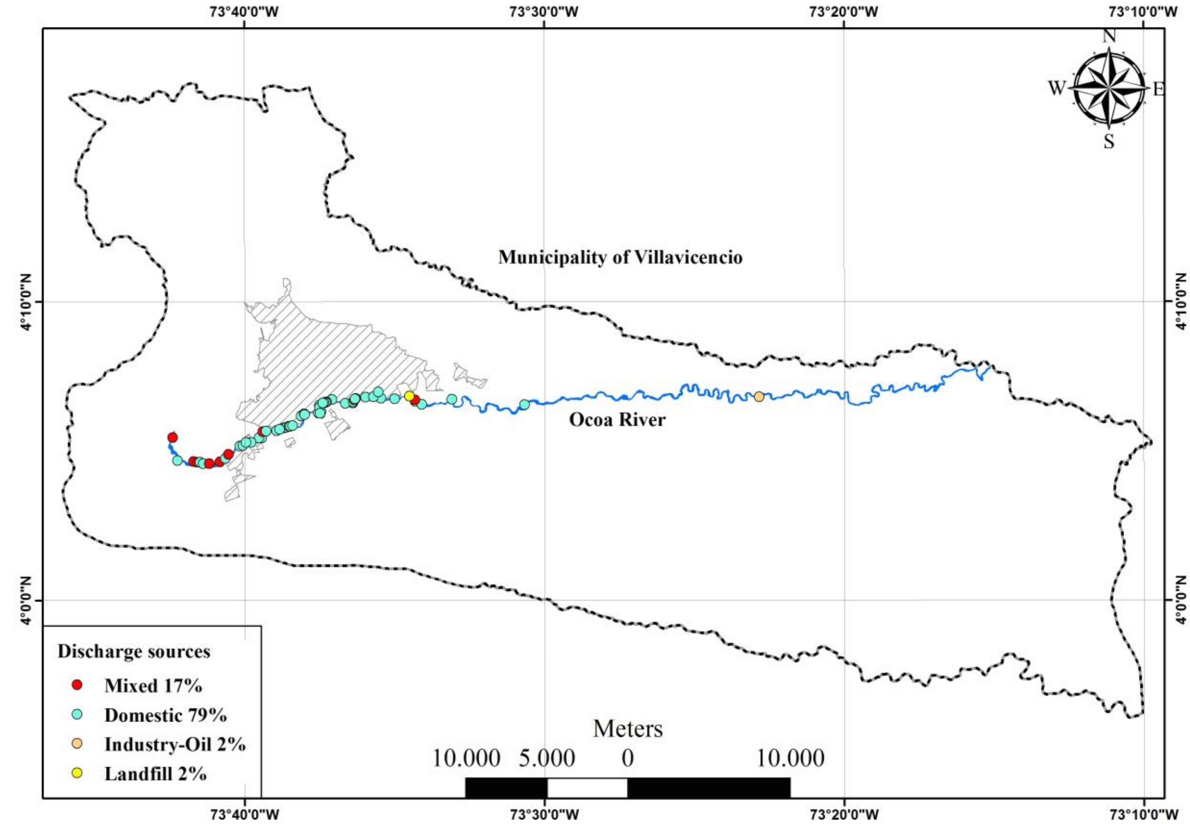

Figure 5.2 Distribution and sources of discharges in the Ocoa River. The stripped pattern shows urban areas

Industrial wastewater often contains high levels of metals, non-metals, and volatile compounds, among other inorganic contaminants (Bos et al., 2010). In general, in developing countries, government entities responsible for managing the proper use of natural resources lack the tools that would allow them to determine the load capacity of their rivers and thus apply proper management protocols for wastewater treatment and set rules for the concentrations and amounts of effluent that are allowed to be discharged into the riverine system (Qadir et al., 2015; WHO, 2006).

Based on the above, the water of the Ocoa River in the city of Villavicencio contains organic and inorganic chemicals from the direct discharges of domestic wastewater, water from mixed sources and industrial sources. This polluted water could potentially affect the health of human communities, the riverine ecosystems and alter the properties of agricultural soils that receive prolonged irrigation from wastewater sources (Brindha and Elango, 2014).

5.3.2. Physicochemical Conditions

Soils in the study area had sand, silt and clay contents that ranged from 20.4% to 42.7%; 25.6% to 43.6% and 23.4% to 41.7%, respectively, with a mean ± standard deviation of 33.23 ± 5.8%; 33.6 ± 4.9% and 33.17 ± 4.6%, respectively. The textural class of the soils in the study area predominantly consisted of clay loam (USDA, 1951). This coincides with the General study of soils and Zoning of Lands, Department of Meta (IGAC, 2004), which describes the soils of the study area as Typic Tropofluvents. These soils have a medium-to-fine texture, with periodic aeration deficits as demonstrated by the presence of gray and brown mottles showing moderate-to-poor drainage, they are susceptible to flooding and are deep to very shallow, strongly acidic and have low fertility (McKeague et al., 1987; Reynolds et al., 2014).

5.3.3. Chemical Analysis

According to the statistical analysis (Table 5.1.), the chemical conditions in the study area and the reference samples showed no significant differences with a 0.95 confidence interval (CI). The organic matter (OM) content averaged 1.45% with a range of 1% to 2%. Organic matter is important in soil because it plays a key role in the formation of aggregates, acidity control, cycling of metallic elements and detoxification of pesticides in soils (Zapata, 2004). In this case, the OM content was very low. The pH ranged from 4 to 5.1 with a mean value of 4.52, classifying the soil as very strongly acidic according to Soil Survey Staff (1993). $Al3+$ averaged 1.15 meq/100 g soil and exchangeable bases averaged 1.22 meq/100 g for $Ca2+$, 0.26 meq/100 g for $Mg2+$, 0 16 meq/100 g for $K+$, and 0.08 meq/100 g for $Na+$. The exchangeable phosphorus averaged 8.45 ppm, ranging between 0.8 and 32.5 and showing high heterogeneity with a coefficient of variation of 103.6%. Most of the metals that were tested (Cu, Zn, Ni, Pb, Cd) were below the detection limits of the equipment used in this study.

The use of wastewater can improve the nutritional content of agricultural soils, which is why wastewaters are used in many countries as an alternative to organic manures, generating a decrease in production costs (Oo et al., 2015; Trujillo-González et al., 2016). The highest phosphorus contents were found in the area where recent agricultural activities had been conducted, while low phosphorus content existed on land that had not been in agricultural use over the past year (Figure 5.3.). This was consistent with Sommer (2006), who argued that soil heterogeneity is related to differences in parent material, climate, topography and management practices. Sinegani et al. (2005) also state that the variability of surface soil in agricultural areas is primarily due to agricultural practices, while the variation in subsoil horizons is governed by pedogenic processes. In this case, phosphorus is added with agricultural activities such as irrigation or fertilization, while in uncultivated areas phosphorus is rapidly leached (Elliott and Jaiswal, 2011). Of the heavy metals considered in this study, only Zn was present at detectable levels with a mean of 65.3 mg/kg, while Cu, Ni, Cd and Pb did not reach the limits of quantification: 4.44, 1.3, 3.73 and 6.58 mg/kg, respectively, in the samples studied. These limits are below the values of phytotoxicity of these metals (Kabata et al., 2007). According to reports by Mapanda et al. (2015), Alobaidy et al. (2010) and Klay et al. (2010), these soils were likely to have high concentrations of heavy metals, because irrigation water mixed with domestic and industrial wastewater discharges had been used on these soils for a long time (>25 years). However, in our study we did not find such high concentrations due to the irrigation practices. In general, chemical conditions determined in the study area were similar to those determined by Rincón and Caicedo (2010), Jamioy-Orozco et al. (2015), and Mahecha-Pulido et al. (2015) in nearby areas where wastewaters are not applied, and are considered typical for soils of the “Piedemonte llanero” of Colombia.

Table 5.1. Descriptive statistics and Student t-test mean difference analysis of the area of interest and the reference area for organic matter (OM, %), available phosphorus (P, ppm), pH, aluminum (Al, meq/100 g soil), and the exchangeable bases calcium (Ca), magnesium (Mg), potassium (K), and sodium (Na) meq/100 g soil.

		OM	**P**	**pH**	**Al**	**Ca**	**Mg**	**K**	**Na**
Area of interest in this study	Mean	1.5NS	8.5 NS	4.5 NS	1.1 NS	1.2 NS	0.3 NS	0.2 NS	0.1 NS
	Minimum	1	0.8	4	0.5	0.2	0.01	0.07	0.04
	Maximum	2	32.5	5.1	2.6	2.2	0.6	0.4	0.1
	Standard deviation	0.3	8.76	0.28	0.57	0,52	0.17	0.07	0.03
	Coefficient of variation %	19.4	103.6	6.2	49.7	42.2	68.4	44.1	34.1
	Number of measurements	21	21	21	21	21	21	21	21
Reference area	Mean	1.4NS	2.5NS	3.9NS	1.2NS	0.3NS	0.2NS	0.1NS	0.06NS
T-student test		0.998	0.999	0.999	0.999	0.998	0.999	0.999	0.998

^{NS}, not significant

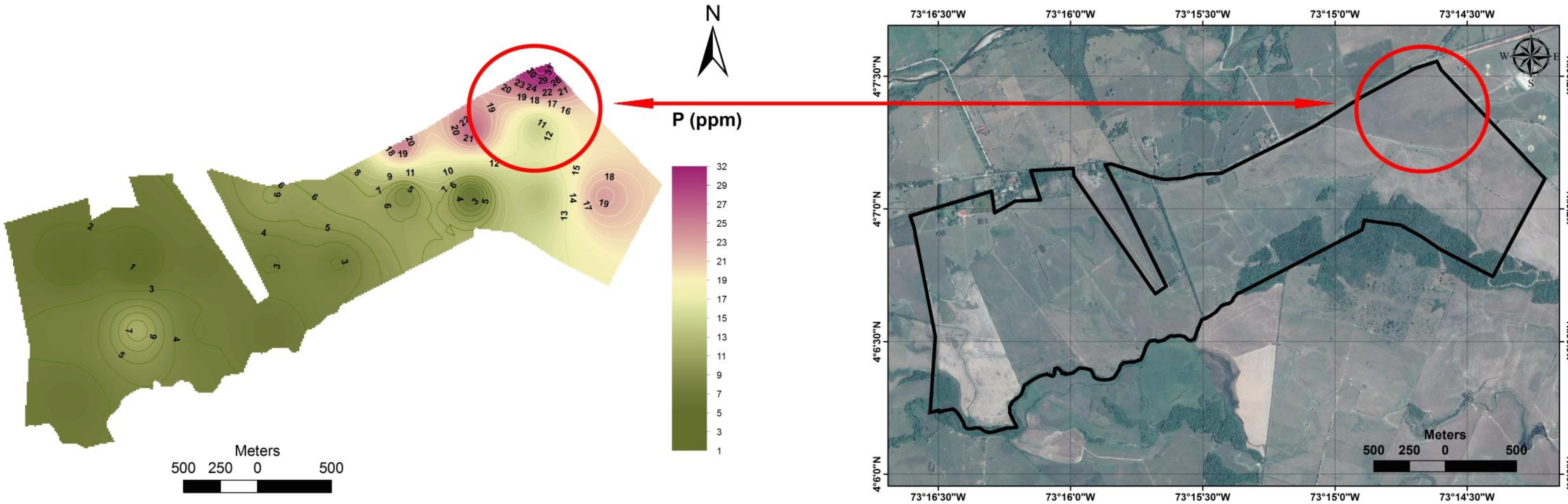

Figure 5.3 Distribution of phosphorus (P) in in the 0–30 cm depth interval (left), satellite image of the study area from Google Earth (right)

Our data show that although these soils have textures that are often associated with nutrient-rich soils, and while they have been irrigated with water that is likely high in organic load, these soils had low nutrient content and have no problems related to heavy metals accumulation in the 0–30 cm depth interval. This may be explained by considering the climatic conditions of the sampling area (abundant rainfall and high temperatures) because different amounts of rain and varying temperatures modify how geomorphological and soil physical and hydrological processes work (Cerdà, 1998). Yang et al. (2015) and Azouzi et al. (2016) suggest that in regions with such high temperatures and rainfall throughout the year, rapid oxidation of organic matter occurs and fast leaching of nutrients and pollutants such as heavy metals is common. Since climate is one of the most important factors determining soil development, vegetation cover, soil type, flora and fauna, processes in the soil such as soil degradation, erosion and loss of nutrients are also related to this (Bockheim et al., 2014; Campos et al., 2014; Cerdà, 2014). Therefore, the most likely explanation for the low nutrient and metal contents is the very rapid processes in the soil due to the intensive climate. It is also possible that the pollutant load in the river was diluted by the river water to the point that the application of the river water as an irrigation source did not significantly impact soil properties. Either of these could explain why the mean differences between the irrigated area and the reference area were not significant.

5.4. Conclusions

Although water exposed to wastewater sources was used for irrigation in the study area, the 0–30 cm interval of soils in the Villavicencio region in Colombia showed no physico-chemical alterations that gave evidence of a change due to the constant use of contaminated irrigation water over a 25+year period. In addition, the behavior of phosphorus demonstrated that recent agricultural activities are important factors when evaluating the physicochemical conditions of these soils. Finally, it is necessary to establish reference values for this region and monitoring strategies to assess any geochemical changes, especially in soils irrigated with effluent-laden waters from various sources.

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6. CONCLUSIONES GENERALES

6. CONCLUSIONES GENERALES

Los resultados de este estudio permiten obtener las siguientes conclusiones:

1. A pesar de que Villavicencio viene a suponer una región vital con acelerado desarrollo económico, se percibe una clara escasez de trabajos publicados relacionados con el efecto de este proceso sobre la calidad ambiental, por lo que los resultados de la presente tesis suponen un avance en esta materia.

2. En Colombia, como en otros países latinoamericanos, la dinámica de las ciudades tipo Villavicencio comienza a mostrar los posibles efectos adversos sobre la salud de las personas y los sistemas naturales, debido fundamentalmente a un escaso control sobre el efecto de la generación de residuos potencialmente contaminantes. En este sentido, la propensión suelos/sedimentos urbanos conforman la base para convertirse en reservorio de contaminantes tales como los denominados elementos potencialmente tóxicos, entre los que cabe destacar los metales pesados.

3. Diferenciando en la Ciudad de Villavicencio tres usos predominantes del suelo suficientemente contrastados (residencial, comercial y vías principales), e investigando los contenidos en metales pesados en polvo vial de los mismos, se descubren los “puntos calientes” por altas concentraciones de metales pesados. Estos puntos calientes, establecidos, mediante un análisis de geo estadística y multivariados, se sitúan en aquellas zonas destinadas al comercio, en concreto a la prestación de servicios de reparación y venta de partes para automóviles con importantes concentraciones de Plomo, Cobre y Zinc.

4. Aunque el contenido de metales puede atribuirse tanto a fuentes geoquímicas como fuentes antrópicas, realmente son estas últimas las que llevan a la contaminación por estos elementos. En este sentido cabe citar el uso histórico de la gasolina con plomo, altamente residual en la superficie vial, y el actual uso de

pinturas con altas concentraciones de estos mismos, alto flujo de vehículos, el estado de las carreteras, el desgaste de los neumáticos, los frenos y el uso de lubricantes.

5. En función del índice de geo-acumulación (Müller) y del índice de riesgo ecológico (Hakanson), estas zonas con elevados contenidos en metales pesados alcanzan la categoría de zonas con moderada a fuertemente contaminación

6. En el análisis efectuado de riesgo de exposición a la salud humana, se encuentra que, en la citada zona de prestación de servicios de reparación de automóviles, el riesgo fue mayor que en otros sectores de la ciudad y, aunque no se alcanzaron los niveles de riesgo, los datos obtenidos suponen una alerta para tomar medidas de mitigación.

7. Como corolario de estos resultados se desprende la necesidad de mejorar los procesos de regulación de los sistemas de gestión de residuos peligrosos en este tipo de actividad comercial.

8. En lo que se refiere a la evaluación del efecto de esta dinámica de la ciudad sobre sus suelos agrícolas periurbanos, se evidenció que el uso continuado, durante más de 25 años, de aguas de riego potencialmente contaminadas con aportes de escorrentía urbana, desechos domésticos e industriales, no ha mostrado alteraciones sustanciales que identifiquen cambios superficiales en dichos suelos agrícolas periurbanos. Esta falta de interacción se atribuye a que la región de Villavicencio es una región ecuatorial, con unas condiciones climáticas singulares, ya que las precipitaciones superan los 3000 mm / año y la temperatura promedio alcanza los 25.6 °C.

9. Los datos obtenidos indican la necesidad de mejorar la comprensión del flujo de estos elementos (origen y destino), como una herramienta para la gestión de

alternativas de gestión ambiental que contribuyan a mitigar efectos negativos sobre la salud humana y los recursos naturales.

10. Se constata que, aunque la ciudad de Villavicencio viene a representar a una ciudad tipo de tamaño medio, en los sectores comerciales se alcanzan concentraciones en algunos contaminantes superiores a los reportados para otras ciudades de mucho mayor tamaño, tradicionalmente consideradas como contaminadas (como es el caso de las grandes ciudades chinas).

11. La dinámica urbana y los sistemas de gestión de residuos se convierten en un determinante clave para garantizar la calidad ambiental de las ciudades y optimizar estrategias como el barrido urbano diferencial según las actividades socioeconómicas que se desarrollen en la misma.

12. Se considera necesario promover estudios encaminados a establecer los valores genéricos de referencia para esta región, al tiempo que deben establecerse estrategias de control o monitoreo para evaluar cualquier cambio geoquímico sustancial, especialmente en aquellos suelos irrigados con aguas cargadas de efluentes de distintos orígenes, pero emanados o ligados a la ciudad.

13. Finalmente, estos resultados conforman una herramienta básica para que las Administraciones Locales, establezcan acciones de planificación, optimización y monitoreo de estrategias de gestión ambiental en ciudades de tamaño medio; de este modo se podrá garantizar la reducción de riesgos tanto sobre la salud pública como en los ecosistemas dependientes.

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